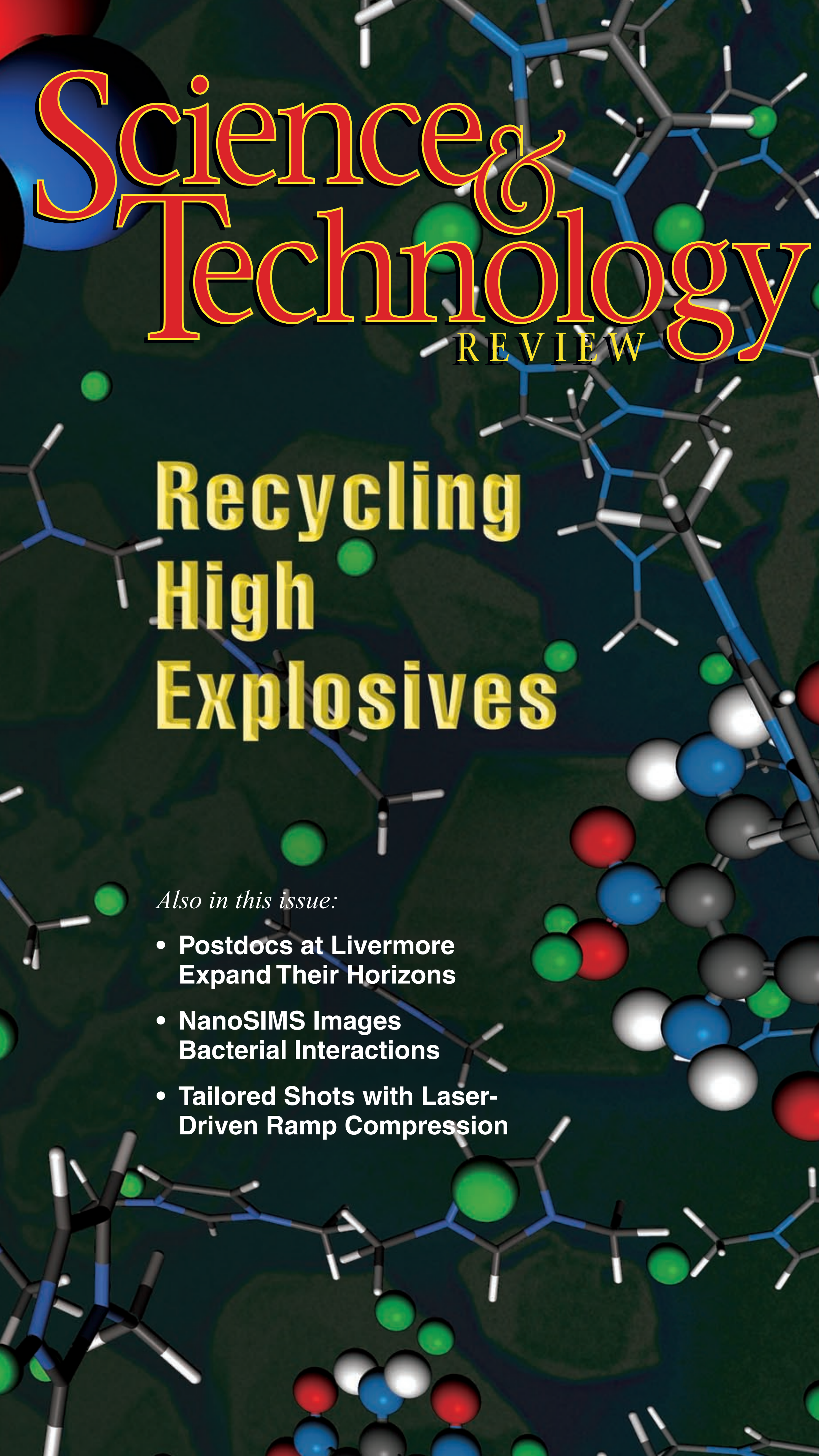
June 2009

Science & Technology REVIEW

National Nuclear
Security Administration's
Lawrence Livermore
National Laboratory



Recycling High Explosives

Also in this issue:

- Postdocs at Livermore Expand Their Horizons
- NanoSIMS Images Bacterial Interactions
- Tailored Shots with Laser-Driven Ramp Compression

About the Cover

The high explosive TATB (1,3,5-triamino-2,4,6-trinitrobenzene) is nearly invulnerable to accidental detonation. Its inherent safety makes TATB a valuable component in the nation's nuclear weapons stockpile, Department of Defense munitions, and explosives for mining and oil production activities. Because TATB supplies are scarce, recycling the material from old nuclear warheads is an attractive option to meet current demands. Livermore scientists have developed a solvent system that uses ionic liquids to dissolve and recrystallize TATB molecules. This "green" system, described in the article beginning on p. 4, produces higher-quality crystals, with better size, shape, and purity, than previous manufacturing techniques. On the cover, a computer rendering shows 1,3-dimethylimidazolium fluoride, one of the ionic liquids evaluated by the Livermore researchers.

Cover design: Daniel Moore

About the Review

At Lawrence Livermore National Laboratory, we focus science and technology on ensuring our nation's security. We also apply that expertise to solve other important national problems in energy, bioscience, and the environment. *Science & Technology Review* is published eight times a year to communicate, to a broad audience, the Laboratory's scientific and technological accomplishments in fulfilling its primary missions. The publication's goal is to help readers understand these accomplishments and appreciate their value to the individual citizen, the nation, and the world.

The Laboratory is operated by Lawrence Livermore National Security, LLC (LLNS), for the Department of Energy's National Nuclear Security Administration. LLNS is a partnership involving Bechtel National, University of California, Babcock & Wilcox, Washington Division of URS Corporation, and Battelle in affiliation with Texas A&M University. More information about LLNS is available online at www.llnsllc.com.

Please address any correspondence (including name and address changes) to *S&TR*, Mail Stop L-664, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94551, or telephone (925) 423-3432. Our e-mail address is str-mail@llnl.gov. *S&TR* is available on the Web at str.llnl.gov.

NNSA
National Nuclear Security Administration
LAWRENCE LIVERMORE NATIONAL SECURITY LLC

Prepared by LLNL under contract
DE-AC52-07NA27344

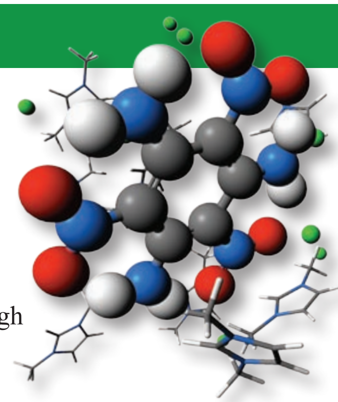
Science & Technology Review

June 2009

Lawrence Livermore National Laboratory

Contents

Features



3 **A Safer and Even More Effective TATB**
Commentary by Bruce T. Goodwin

4 **Dissolving Molecules to Improve Their Performance**
Computer scientists and chemists have teamed to develop a green method for recycling a valuable high explosive that is no longer manufactured.

11 **Exceptional People Producing Great Science**
Postdoctoral researchers lend their expertise to projects that support the Laboratory's missions.

Research Highlights

19 **Revealing the Identities and Functions of Microbes**
A new imaging technique illuminates bacterial metabolic pathways and complex relationships.

22 **A Laser Look inside Planets**
Laser-driven ramp compression may one day reveal the interior structure of Earth-like planets in other solar systems.

Departments

2 The Laboratory in the News

24 Patents and Awards

25 Abstracts

S&TR Staff

Scientific Editor
Jane P. Bearinger

Managing Editor
Ray Marazzi

Publication Editor
Carolin Middleton

Writers
Arnie Heller, Caryn Meissner, and Katie Walter

Art Director
Daniel Moore

Proofreader
Pamela MacGregor

Print Coordinator
Charlie M. Arteago, Jr.

S&TR, a Director's Office publication, is produced by the Technical Information Department under the direction of the Office of Planning and Special Studies.

S&TR is available on the Web at str.llnl.gov

Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

UCRL-TR-52000-09-6
Distribution Category UC-99
June 2009

Simulations Reveal Unexpected Melt State in Metals

Molecular dynamics simulations conducted by a team of Livermore researchers indicate that at high pressures, a metal transforms into a gooey substance before it melts into a liquid as the temperature increases. The calculations, which were run on the Laboratory's BlueGene/L supercomputer, examined the metal tantalum, but the results suggest that this plastic flow state may occur in other metals as well.

Previous research assumed that solid metals immediately turn into a liquid when exposed to high pressures and temperatures. In the Livermore simulations, tantalum underwent a viscous plastic flow transition under heating and shear strain, the deformation process in which applied pressure causes the parallel internal surfaces of a material to slide past one another. "The viscous material was much like hot tar," says materials scientist Christine Wu, who led the research team in Livermore's Physical and Life Sciences Directorate. "It flowed as a group, not as the individual atoms observed in liquid flow."

Distinguishing the transformation process between liquid and plastic flow will help researchers better understand how metals behave under high pressures. For example, says Wu, "This general phenomenon could apply to iron and have implications for the structure of Earth's core." She notes, however, that further experiments are needed to verify the simulations. Wu and her Livermore colleagues Per Söderlind, James Glosli, and John Klepeis published their results in the March 2009 issue of *Nature Materials*.

Contact: Christine Wu (925) 424-4096 (wu5@llnl.gov).

Corals May Be Oldest Living Marine Organism

Researchers from Livermore, the University of California at Santa Cruz, and Stanford University have determined that two groups of Hawaiian deep-sea corals are far older than any previously recorded. The team collected samples from the Makapuu and Lanikai deep-sea coral beds off the coast of Oahu, from the Keahole Point deep-sea coral bed off the coast of the Big Island, and from the Cross Seamount about 160 kilometers south of Oahu. Laboratory scientists Tom Guilderson and Stewart Fallon, working at the Center for Accelerator Mass Spectrometry, performed radiocarbon (carbon-14) dating to determine the ages of two species: *Geradia* (gold coral) and *Leiopathes* (deep-water black coral). The longest-lived samples were 2,740 years and 4,270 years, respectively. Results from this study appeared in the March 31, 2009, edition of the *Proceedings of the National Academy of Sciences*.

The deep-water black coral is the oldest living skeletal-accreting marine organism known. "To the best of our knowledge, it is the oldest colonial organism yet found," says Guilderson. "The carbon-14 data indicate that the living polyps are only a few years old, or at least their carbon is, but they have been continuously replaced from centuries to millennia while accreting their underlying skeleton."

Deep-sea corals grow on seamounts and continental margins at depths of 300 to 3,000 meters. These communities are hot spots of biodiversity, providing critical habitat for fish and invertebrates, but their survival is threatened by changing ocean conditions and by commercial activities such as fishing and harvesting corals for jewelry. By better understanding the ecology of deep-sea corals and their interrelationships with associated communities, researchers can guide decision makers in developing conservation strategies for these important habitat-forming species.

Contact: Thomas Guilderson (925) 422-1753 (guilderson1@llnl.gov).

Brightest Galaxies Grew Early after Big Bang

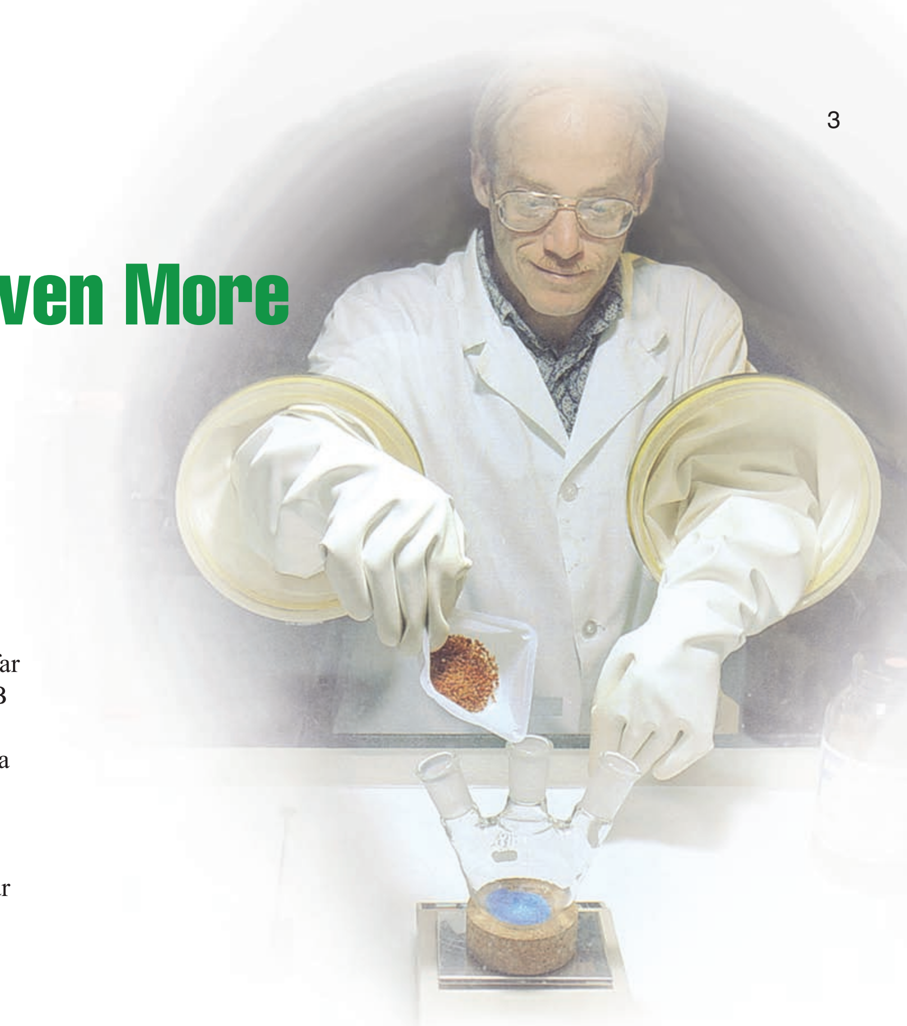
Research by an international team of astronomers, including Adam Stanford at Livermore's Institute of Geophysics and Planetary Physics, provides a new picture of how galaxies formed after the big bang. The team's results indicate that the stellar mass of the largest galaxies, called bright cluster galaxies, experienced an early period of rapid growth 9 billion years ago. In fact, these galaxies acquired more than 90 percent of their final stellar mass within the first 4 billion years after the big bang.

The international collaboration used infrared wavebands to determine the ages of stars within a galaxy. Infrared wavebands are less sensitive than optical light to the presence of young stars. As a result, they can more accurately trace an old stellar population within a galaxy and measure its mass.

Scientific consensus is that galaxies begin as small density fluctuations in the early universe. Stars form in subgalactic-size building blocks called haloes and merge over time, in effect swallowing up other galaxies that come too close. The team found that despite feeding on a constant diet of small galaxies, the heaviest galaxies have not increased their mass during the last 9 billion years. In a universe that is 13.7 billion years old, these results will likely spark a debate on the process of galaxy evolution. The team reported on its study in the April 2, 2009, issue of *Nature*.

Contact: Adam Stanford (925) 423-6013 (stanford3@llnl.gov).

A Safer and Even More Effective TATB



A little molecule called 1,3,5-triamino-2,4,6-trinitrobenzene, or TATB, is one of the most important materials in modern nuclear weapons. A powerful explosive, TATB is key to the detonation process in about one-third of the weapons in the nation's stockpile. TATB is extremely difficult to detonate. As far as I know, no natural force on Earth will make it explode. TATB can be slammed into a wall or have a bullet shot through it, and it will not explode. From a safety standpoint, it has no peers as a high explosive.

TATB is especially important today. When the Soviet Union was our enemy, conventional high explosives—assuming proper handling procedures—were perfectly adequate in nuclear weapons. Today, however, our enemies are willing to sacrifice themselves to obtain materials that can inflict deadly harm on others. Our enemies are a patient lot and strive for any means to inflict terror, from "dirty" bombs to nuclear explosives. Maintaining the safety and security of our nuclear weapons is more important than ever, and TATB is central to every aspect of this mission.

The Departments of Energy and Defense both need a new source of TATB for use in remanufactured weapons. Very little TATB exists today, and none is being manufactured because of environmental regulations. As part of the Transformational Materials Initiative funded by the Laboratory Directed Research and Development Program, resourceful Livermore scientists have found just such a source.

Their solution, described in the article beginning on p. 4, turns out to be recycled TATB, made usable by combining old TATB with a unique solvent. Remarkably, the recycled TATB is a much more effective product than the original, with better crystal quality, size, shape, and purity. And the new product is less expensive to manufacture than the cost to purchase TATB out of shrinking stores.

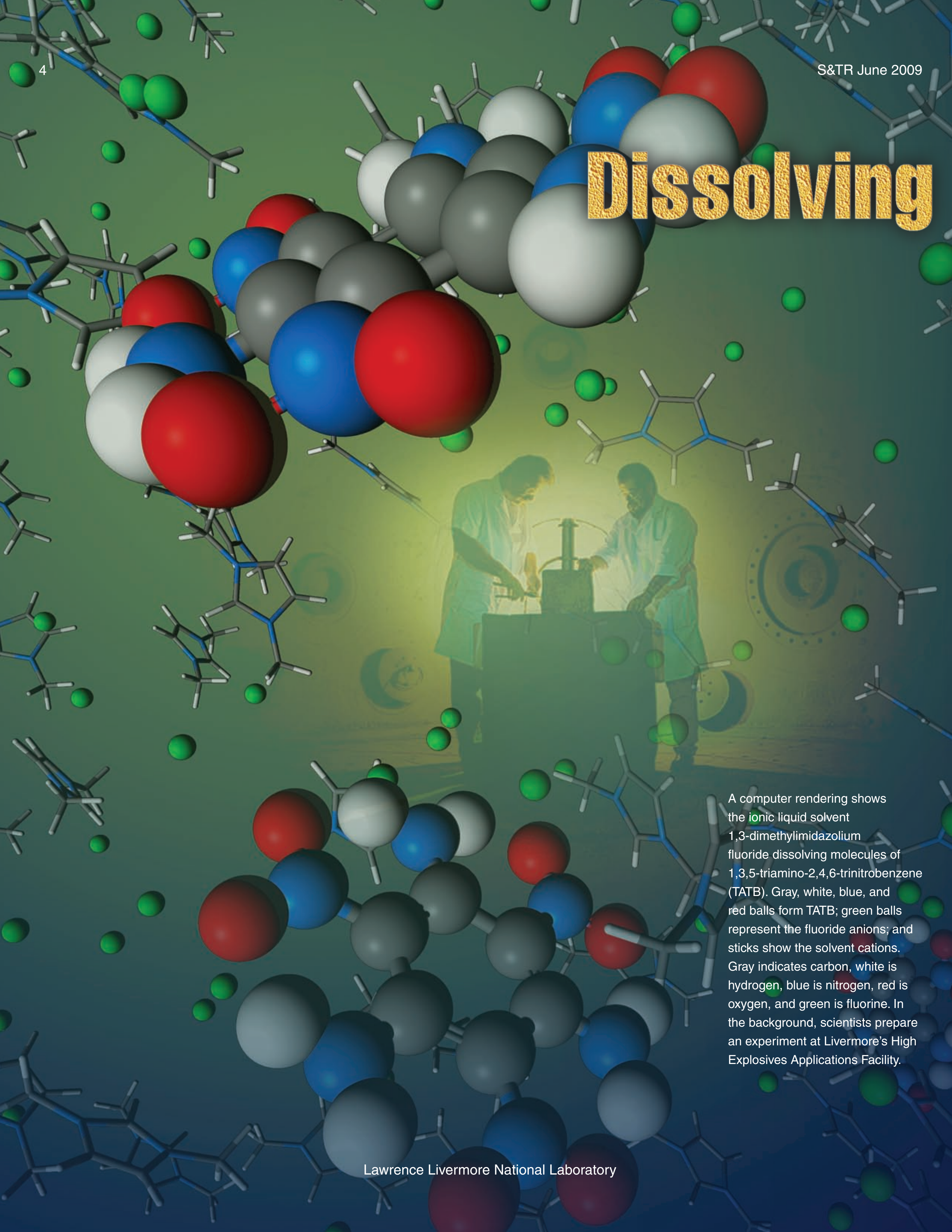
The solvent is an ionic liquid. Many varieties of ionic liquids exist, and they have proved useful for more than a decade at dissolving all sorts of hydrogen-bonded solids. Ionic liquids, sometimes called green solvents, do not evaporate if left out and thus do not contribute to air pollution. They are recyclable as well. Livermore researchers were the first to use an ionic liquid to dissolve a high explosive.

The National Nuclear Security Administration and its national laboratories are stewards of the nation's nuclear stockpile, and the new TATB makes our life much easier. Better crystal quality and more uniform crystallization translate into a safer TATB, one that is even more difficult to detonate. The new TATB is thus a crucial discovery for the Department of Energy, which uses thousands of pounds of high explosives each year.

Recycled TATB is even more important for the Department of Defense, which consumes millions of pounds of high explosives every year in all kinds of conventional weapons. Today, TATB is used only occasionally in certain munitions because of its expense. However, a cheaper TATB and one that is safer to boot could bring about its use in a far broader range of conventional weapons. The American soldier would be safer, the most important goal of all.

The TATB discovery is unique even by Laboratory standards. It uses a 15-year-old solvent that is "green" by every measure to recycle and even improve a precious weapons resource. This technical discovery is a testament to the never-ending innovation here and represents a triumph for the Laboratory's stockpile stewardship program and the Transformational Materials Initiative.

■ Bruce T. Goodwin is principal associate director for Weapons and Complex Integration.



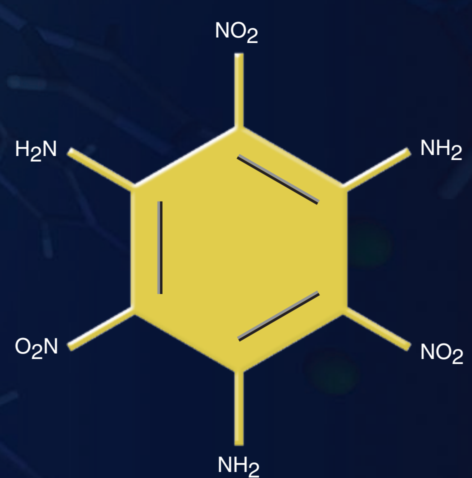
Dissolving

A computer rendering shows the ionic liquid solvent 1,3-dimethylimidazolium fluoride dissolving molecules of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Gray, white, blue, and red balls form TATB; green balls represent the fluoride anions; and sticks show the solvent cations. Gray indicates carbon, white is hydrogen, blue is nitrogen, red is oxygen, and green is fluorine. In the background, scientists prepare an experiment at Livermore's High Explosives Applications Facility.

Molecules to Improve Their Performance

Combining computer modeling and laboratory synthesis, researchers have developed a green method to recycle a valuable and scarce explosive.

FROM space dust to rare isotopes, Lawrence Livermore researchers work with many unusual and exotic materials. Among the most remarkable is a molecule called 1,3,5-triamino-2,4,6-trinitrobenzene, or TATB. Used as a high explosive, TATB is nearly invulnerable to significant energy release from plane crashes, fires, and explosions or to deliberate attack with a small firearm. TATB's extreme insensitivity to impact, shock, and heat make it a valuable component in about one-third of the nation's nuclear weapons, in some Department of Defense (DoD) munitions, and in explosives used by mining and oil production companies. (See the box on p. 6.)



In the six-sided ring structure of TATB, nitro compounds (NO_2 and O_2N) alternate with amine compounds (H_2N and NH_2).

TATB has not been produced for more than two decades primarily because of environmental regulations. As a result, DoD has been purchasing old TATB from Department of Energy (DOE) stockpiles while new, greener manufacturing methods are being developed.

The scarcity of TATB makes recycling the material from old nuclear warheads an attractive option. In any recycling process, TATB molecules must be separated from the polymer binder (the plastic "glue" binding the crystals), dissolved, and then recrystallized to the correct microscopic crystal size and shape. These steps are necessary to produce a recycled material with the same performance characteristics as new material. Until recently, a TATB recycling process was not available because effective solvents did not exist.

In response to urgent needs for replenished supplies of high-quality TATB, Livermore scientists have developed 3-ethyl-1-methylimidazolium acetate–dimethyl sulfoxide, a solvent system that belongs to a class of powerful but environmentally benign compounds called ionic liquids. This system has produced TATB with better crystal quality, size, shape, and purity than previous manufacturing techniques have produced. What's more, the crystals have a uniform size that can be controlled when TATB molecules are recrystallized out of solution. The new system may also have applications for efficiently converting cellulose and other difficult-to-dissolve organic compounds, such as cornstalks, into biofuels.

Focus on Advanced Materials

The TATB development effort was supported under the Transformational Materials Initiative (TMI), which was funded by Livermore's Laboratory Directed Research and Development Program. Begun in 2006, TMI focused on advanced materials for the nation's future nuclear stockpile. Its charter includes addressing critical issues such as the dwindling supply of high-quality TATB. The TMI-sponsored research on TATB was featured on the covers of the January 2009 issue of *New Journal of Chemistry* and the September 1, 2008, issue of *Physical Chemistry Chemical Physics*.

"TATB is a precious resource," says TMI leader Robert Maxwell. "If we could recycle it when we disassemble warheads, we could save the nation many millions of dollars. However, we need exactly the right purity, particle size, and shape of TATB crystals to ensure the highest safety and performance standards."

Under the microscope, TATB particles taken from old warheads appear disorganized, with varying shapes and sizes—not the well-faceted crystals chemists require to confidently predict performance and safety. Chemist George Overturf, high explosives subject-matter expert for the Laboratory's weapons program, notes, "We need TATB to be reconstituted back to the original particle specifications."

Some experts are concerned that in its current formulation, recycled TATB could harbor an excessive number of "hot spots," microscopic voids located within crystals or at the interfaces with particles of binder. Voids tend to heat up, which could reduce TATB's insensitivity to shock. "Keeping the molecules tightly packed means greater insensitivity to shocks," says chemist Yong Han, lead author of the *New Journal of Chemistry* article.

The Livermore team, drawn from the Weapons and Complex Integration Principal Directorate and the Physical and Life Sciences Directorate, focused on developing a method that controls the size and shape of crystals as they are reconstituted from old TATB. The effort included work at the Laboratory's High Explosives Applications Facility and Site 300, the experimental test site about 24 kilometers east of Livermore's main site. Computer modeling also helped guide the chemists' synthesis efforts. The result is a patented process that improves the quality of recycled TATB and can be

Simulations to Measure Sensitivity

Some high explosives such as trinitrotoluene (TNT) are easily detonated. Others such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which is used in some of the nation's nuclear weapons, are insensitive to shock, heat, or impact and thus are difficult to detonate accidentally. High explosives have held tight to their secrets about why some are insensitive and safe and others very sensitive. "Despite the extensive production and use of explosives for more than a century, their basic microscopic properties during detonation have yet to be unraveled," says Laboratory physicist Evan Reed.

Two years ago, Reed led a team that performed the first-ever quantum molecular dynamics (QMD) simulations of a high explosive's detonation front. This first test case studied nitromethane, a fairly simple molecule and a high explosive of moderate sensitivity. Almost as energetic as TNT, nitromethane is oxygen poor. However, when mixed with ammonium nitrate, as it was in the 1995 bombing of the Alfred P. Murrah Federal Building in Oklahoma City, it can be extremely lethal.

A QMD simulation of only 0.2 nanoseconds revealed that nitromethane undergoes a totally unexpected change during detonation. First, it decomposes chemically and then transforms into a semimetallic state for a short distance behind the detonation front. Nitromethane is an optically transparent, electrically insulating material. Yet, for a brief moment, it turns into an optically reflecting conductor before returning to its transparent, insulating state. New experiments based on this simulation are designed to send shock waves into nitromethane to measure changes at the detonation front. "The challenge at the moment," says Reed, "is matching the shock pressure of the experiment to the pressure used during the QMD simulation."

A more recent set of QMD simulations by Reed and Riad Manaa examined TATB. "We were looking for a possible explanation for its lack of sensitivity," says Reed. The simulations show for the first time that, during detonation, TATB's numerous carbon and nitrogen atoms form big, viscous globs, known as heterocycles. Atoms of nitrogen, the ingredient in explosives that makes them boom, must diffuse out of the carbon globs before they can release their energy to power the detonation process. In contrast, nitromethane breaks down quickly into small molecules rather than viscous globs. The discovery of these globs may explain TATB's long reaction time.

used as a last step in any new production method to ensure that quality standards are met.

Molecular Crystals Tightly Packed

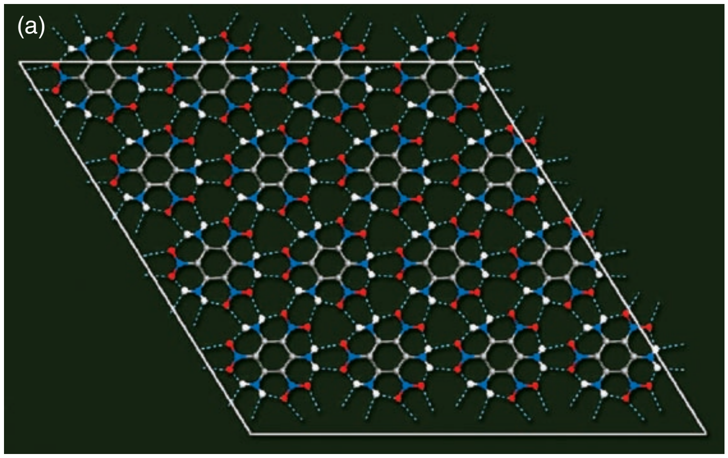
Like most high explosives, TATB belongs to a class of materials called molecular crystals, which are made of electrically neutral molecules that are tightly packed together. Materials made from molecular crystals include drugs, pigments, agricultural chemicals, and active components in optoelectronics.

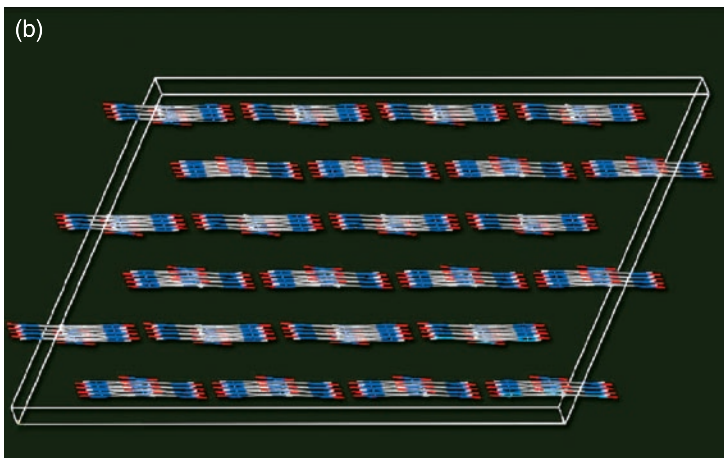
Molecular crystals are often bound together by a strong network of hydrogen bonds in which an electronegative atom is attracted to a positively charged hydrogen atom bonded to another electronegative atom. Hydrogen bonds also link TATB molecules together in well-defined layers. (See the figures at right.)

TATB is one of the most strongly hydrogen-bonded solids known. As a result, it is extremely insoluble in common solvents, even at high temperatures. Dimethyl sulfoxide (DMSO), the best conventional organic solvent for TATB, dissolves only 70 parts per million and is difficult to remove from solution. "Super" acids, such as concentrated sulfuric acid, can dissolve much more TATB at room temperature than DMSO, but they are dangerous to work with. They also can degrade the TATB molecular structure and thus weaken insensitivity to shock.

Keeping in mind that TATB's hydrogen bonds must be broken in a chemically benign manner, the Livermore team focused on ionic liquids. Ionic liquids have proved useful for dissolving hydrogen-bonded solids such as natural fibers. One example is cellulose, a biorenewable material with applications to the paper, fiber, membrane, polymer, and paint industries. Ionic liquids had not previously been considered as candidates for dissolving high explosives, although they are known to be powerful breakers of hydrogen bonds.

"Researchers are excited about ionic liquids," says Larry Fried, who leads Livermore's extreme chemistry group. "It's one of the most rapidly growing areas in chemistry. More than 1,000 papers are published on this topic every year."





(a) Hydrogen bonds (dotted lines) tightly link TATB molecules to each other within a single layer. (b) These bonds are also responsible for connecting TATB's well-defined layers.

Ionic liquids are a kind of salt, compounds that combine a cation (positively charged ion) with an anion (negatively charged ion). Because so many combinations of cations and anions are possible, the number of different ionic liquids is nearly infinite. Many of them feature a cation based on a molecule called imidazolium, which forms part of many biological molecules, and an anion with a halogen atom such as fluorine, chlorine, or bromine.

Scientists believe the ionic liquid anion breaks TATB hydrogen bonds by pulling individual molecules away from the molecular crystal. In contrast, the ionic liquid's cation has more subtle effects. "It's more like a spectator," says Fried.

Ionic liquids are also attractive because they offer reduced environmental and safety concerns compared to other solvents. As a result, they are sometimes called green solvents. The ionic liquids considered for use as solvents melt at 100°C or below, and many of them are liquid at room temperature. In addition, they have no vapor pressure—that is, they do not evaporate if left out and thus do not contribute to air pollution. Another advantage is that they are recyclable. Finally, their stability at high temperatures provides an added measure of safety.

Modeling Finds a Good Match

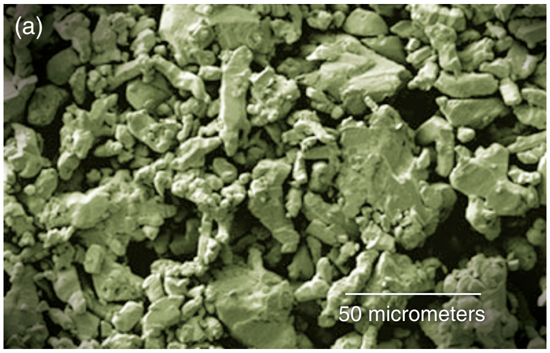
Because ionic liquids containing chloride anions are effective solvents, the team first considered these compounds as candidates for dissolving TATB. In particular, the team investigated 3-butyl-1-methylimidazolium chloride, known to dissolve cellulose and silk and wool fibers. However, it proved ineffective at dissolving TATB. Similar results were observed for other ionic liquids containing chloride anions.

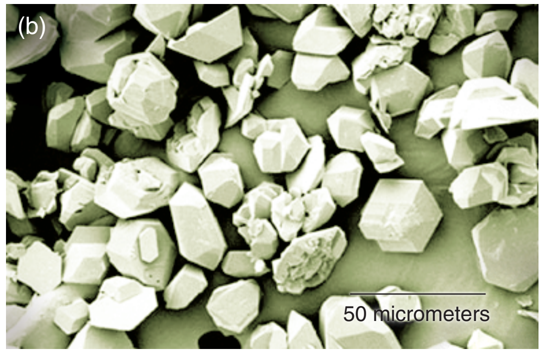
To narrow the possible solvent choices, computational physicist Amitesh Maiti used advanced quantum mechanical simulations. "Synthesizing new ionic liquids and then accurately measuring their solubility are time-consuming and expensive," says Maiti. "Computer simulations can be a much faster and cheaper alternative for screening potentially efficient solvents."

For this effort, Maiti adopted a two-step procedure. The first step applies a quantum mechanical density functional theory approach to compute the electronic charge density of individual solute and solvent molecules—in this case, a TATB molecule and the constituent ions of the candidate ionic liquid. In the second step, a realistic solvation model called COSMO-RS simulates TATB in different ionic liquid environments and uses the results to estimate the extent to which TATB is likely to be dissolved. "We realistically mimic the solvent environment without needing thousands of molecules," he says. "In this way, we can efficiently screen a large number of solvents in a reasonable amount of time."

The modeling effort identified a class of ionic liquids containing fluoride anions that theoretically seemed excellent at dissolving hydrogen bonds, with predicted TATB solubility more than

Chemists (a) Phil Pagoria and (b) Yong Han (front) and Pat Gallagher work at Site 300, the Laboratory's remote experimental test site, to produce TATB solvents for testing.





Images taken with a scanning electron microscope reveal the shape of TATB crystals (a) before and (b) after recrystallization with the ionic liquid 3-ethyl-1-methylimidazolium acetate.

100 times better than the best conventional solvents. Experiments using some of these combinations soon followed, and the measured solubilities compared well with the theoretically computed values, with differences ranging from a factor of 2 to within just a few percent. "We were encouraged to see the excellent agreement between theory and experiment over a broad range of temperatures and solubility values," says Maiti.

With fluoride established as the most efficient anion, the researchers looked for a matching cation to maximize solubility. Calculations pointed to 1,3-dimethylimidazolium as the best match. However, because that molecule has a high melting temperature, the team worked with a related, but slightly larger cation: 1-butyl-3-methylimidazolium. When synthesized, this ionic liquid successfully dissolved TATB, producing large, defect-free crystallites. The solubility of the new material proved roughly 200 times greater than that achieved with DMSO.

The team compared scanning electron microscope images of available TATB with material recrystallized using the ionic liquid. The superior quality of the newly recrystallized TATB was clearly evident in the uniform, well-faceted crystals.

Using x-ray diffraction and nuclear magnetic resonance, the researchers extensively characterized solid TATB and the TATB–ionic liquid solution to decipher how 1-butyl-3-methylimidazolium fluoride works as a solvent. Experimental images and computer calculations showed that the individual fluoride ions are stabilized (that is, they remain as distinct, chemically unreacted ions) in the presence of coordinating water molecules. Such anions, being strong hydrogen-bond acceptors, disrupt the network of TATB molecules in its crystalline phase and lead to efficient dissolution. In contrast, ionic liquids using chlorine are weaker at breaking hydrogen bonds and are ineffective in the presence of even a small amount of water.

An Even Better Solvent

Although 1-butyl-3-methylimidazolium fluoride was an effective TATB solvent, it proved unstable and difficult to work with, and its solubility decreased when it was exposed to water from air. Also, it is not readily available commercially, thereby increasing costs.

The chemists turned to ionic liquids with anions that contain acetate, while retaining the imidazolium family of cations. Acetate is a cheap chemical, less toxic than fluoride and known for breaking hydrogen bonds. It is also easy to work with because it does not absorb water. Guided by Maiti's modeling results, chemists tested several formulations, using both commercially available and custom-synthesized ionic solvents.

Three-ethyl-1-methylimidazolium acetate (EMImOAc) showed a surprisingly good solubility of TATB, almost as good as 1-butyl-3-methylimidazolium fluoride. In experiments performed by Phil Pagoria, leader of advanced materials synthesis, an EMImOAc–TATB mixture was heated to 100°C and maintained at this temperature until all of the particles dissolved. Over time, single TATB crystals appeared and grew larger as they slowly cooled to room temperature. These crystals were far more uniform in size and shape than the starting TATB crystals. (See the figures above.)

However, the viscosity of EMImOAc at room temperature made the recrystallized TATB difficult to filter. "Ionic liquids can be very viscous, like honey or molasses," says Fried. To reduce the viscosity, the research team added DMSO, the long-standing (but not particularly effective) solvent for TATB. As expected, mixing DMSO with EMImOAc lowered the solubility of TATB proportionate to the concentration of DMSO. However, a solution with as much as 80 percent (by weight) of DMSO dissolved a significant amount of TATB and reduced material costs appreciably.

Controlling Crystallization

Electron micrographs of the recrystallized TATB crystals showed good morphology compared to the starting material, with sizes ranging from 10 to 50 micrometers in diameter. However, at room temperature, some of the TATB remained in solution. As a result, the chemists investigated using acetic acid (purified vinegar) as an "antisolvent." Experiments showed that by varying the concentration of acetic acid and the rate at which it is added, they could control the size of the recrystallized crystals. Adding acetic acid slowly resulted in larger (100-micrometer-diameter) crystals, while adding it faster produced smaller (10-micrometer-diameter) crystals. "We want both sizes—larger crystals to take up most of the volume, and smaller crystals to fill in the gaps between the larger ones," says Han. "This combination produces the highest density material when TATB is pressed into parts with the plastic binder."

The chemists have subjected the recrystallized TATB to a battery of tests, with excellent results. They have also used nuclear magnetic resonance and Raman spectroscopy to investigate exactly how EMImOAc dissolves TATB.

"We now have a process where we can control the size and morphology of TATB crystals," says Fried. "Before, they looked like misshapen crystals. Now, they look like well-faceted jewels with far fewer defects." (See the figure below.) With the Livermore technique, TATB from any source and of unknown quality can be purified and standardized.

Randy Simpson, a high-explosives expert, underscores the significance of the Livermore research effort. "Rarely do scientists achieve this degree of improvement so quickly in any field of research," he says.

Other Applications

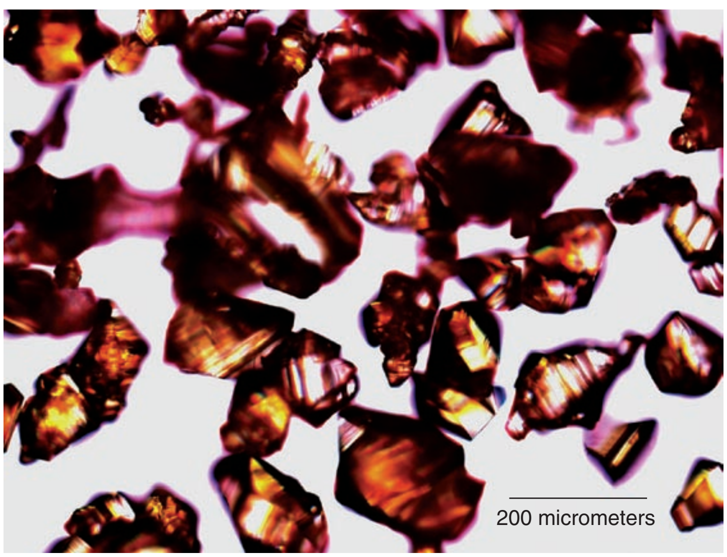
The TMI researchers have presented their findings at scientific conferences and are optimizing how to transfer the process to DOE and DoD materials experts, who are working to restart TATB production lines. In the meantime, the research team is studying whether the quality of other insensitive high explosives, such as LLM-105, could be improved by the same dissolution–recrystallization process.

Maxwell notes that many industries using hard-to-dissolve materials, especially hydrogen-bonded materials, might benefit from the Livermore research results. For example, in tests of the EMImOAc–DMSO solvent combination on cellulose, the team obtained solubilities comparable with those reported using chloride-based ionic liquids. Simpson points out that the ethanol industry uses ears of corn as feedstock, leaving behind much of the cornstalk. With the right solvent, cornstalks could be added to the mixture, markedly increasing the amount of ethanol in the marketplace and reducing production costs. Other potential applications include producing plastics, pharmaceuticals, paints, and propellants.

For his part, Maiti is applying his computer modeling experience to designing ionic liquids for carbon sequestration research. One day, carbon dioxide generated by fossil fuel power plants could be trapped at the smokestack, dissolved in an ionic liquid, filtered, pressurized into a dense stream, and then stored in a repository.

Maxwell says that an important result of the ionic liquid research effort was demonstrating the utility of combining computer modeling with traditional "benchtop" chemistry. Clearly, such a marriage has a long and profitable future.

—Arnie Heller



This optical micrograph shows recrystallized TATB molecules.

Key Words: high explosive, High Explosives Applications Facility, hydrogen bond, ionic liquid, molecular crystal, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), quantum molecular dynamics (QMD), Site 300, Transformational Materials Initiative (TMI).

For further information contact Robert Maxwell (925) 423-4991 (maxwell7@llnl.gov).

Exceptional People Producing Great Science

With passion and skill, postdoctoral researchers apply their talents to the Laboratory's scientific and technical endeavors.

WANTED: Postdocs looking to pursue careers in science and technology. Must be willing to excel and expand their horizons by working with experts and contributing to world-class research. Opportunity awaits at Lawrence Livermore National Laboratory.

In any given year, Livermore is home to 110 to 150 postdoctoral researchers. Known as postdocs, these exceptional people—physicists, chemists, biologists, engineers, and mathematicians, to name a few—lend their scientific expertise to programs across the Laboratory. They come from all over the country and in some cases from abroad within the first five years after receiving a doctoral degree. As part of the Laboratory's Postdoc Program, they get hands-on experience while working closely with scientific leaders and colleagues in their chosen disciplines.

Typically, postdocs apply online for open positions in one of Livermore's four mission-related principal directorates: Science and Technology, which includes Computation, Engineering, and Physical and Life Sciences; Global Security; Weapons and Complex Integration; and National Ignition Facility (NIF) and Photon Science. Ultimately, candidates are selected for their knowledge and capabilities. "These assignments last approximately two years with the possibility of being extended to a third year," says Kris Kulp, director of the Institutional Postdoc Program Board, which oversees the program. After this initial term, some postdocs remain on the scientific staff at the Laboratory, while others head out into academia or industry. "Although we often want our postdocs to stay," says Kulp, "our basic goal is to provide an experience that prepares them well for any job they may have in the future."

Postdocs are integral to the complex work performed at the Laboratory. Almost 80 percent of these researchers receive support from the Laboratory Directed Research and Development (LDRD) Program, which applies internal research and development funds to forward-thinking, potentially high-payoff projects at the forefront of science. Their projects range from predicting California's future climate, supporting stockpile stewardship, and uncovering the secrets of the cosmos to building quantum computers, improving damage mitigation processes for laser optics, characterizing bacteria and spores, and revealing rare particle decays. Their work contributes to the Laboratory's important missions, and they bring a vibrancy and zeal to their research that only improves their chances of success. Says Kulp, "Postdocs have the energy, spark, and enthusiasm that gets translated into great science."

Building California's Climate Record

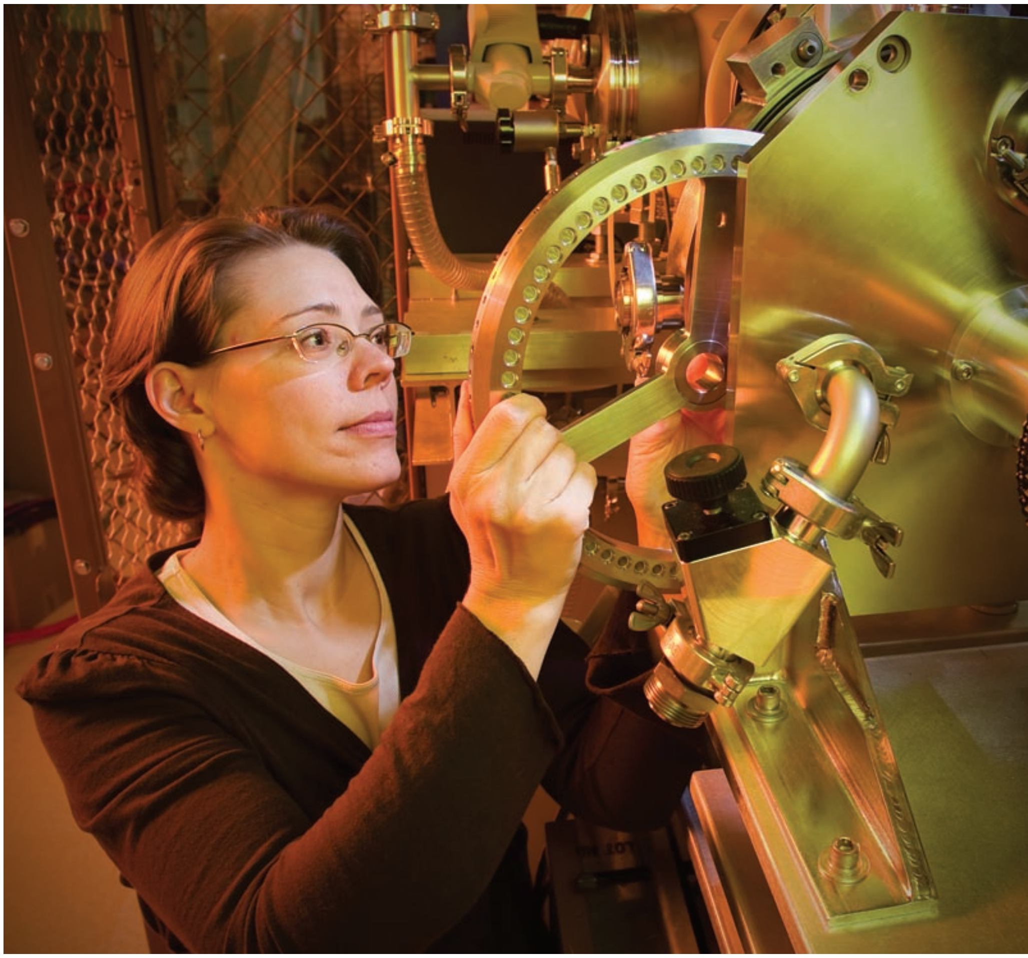
As part of the Laboratory's efforts to predict future climate change, Susan Zimmerman is spearheading a project to develop high-precision paleoclimate records for use in regional climate models. Current models typically use data for only the last 150 years and, thus, miss wet and dry periods from past millennia.

"Remarkably, over the last century, the West has been relatively wet compared to the average for the last 2,000 years," says Zimmerman, who received a Ph.D. in earth sciences from Columbia University. "Without more long-term data, predictive modeling is biased toward these anomalously wet conditions."

With funding from the LDRD Program, Zimmerman is working with researchers across California to analyze lake sediments and develop records that span the last two millennia. "Lakes are long-lived, wet areas where materials are continually deposited over time," she says. Data from these records will be used to map previous drought patterns in California and help climate modelers more accurately simulate the range of natural climate changes. With this information, state agencies can determine the infrastructure needed to meet future demands for water.

"An important part of my effort is building a network of collaborators who are already working on paleoclimate records in different areas of the state," says Zimmerman. She and her colleagues collect samples from natural outcrops such as stream cuts or fault scarps or from vertical cores of sediment extracted from a basin. Layers in the core indicate the conditions under which the sediment was deposited.

Zimmerman analyzes samples at the Laboratory's Center for Accelerator Mass Spectrometry, where she works with Livermore scientists Tom Guilderson, Tom Brown, and Graham Bench, the center's director. Zimmerman pretreats each sample, which may be charcoal, pine needles,

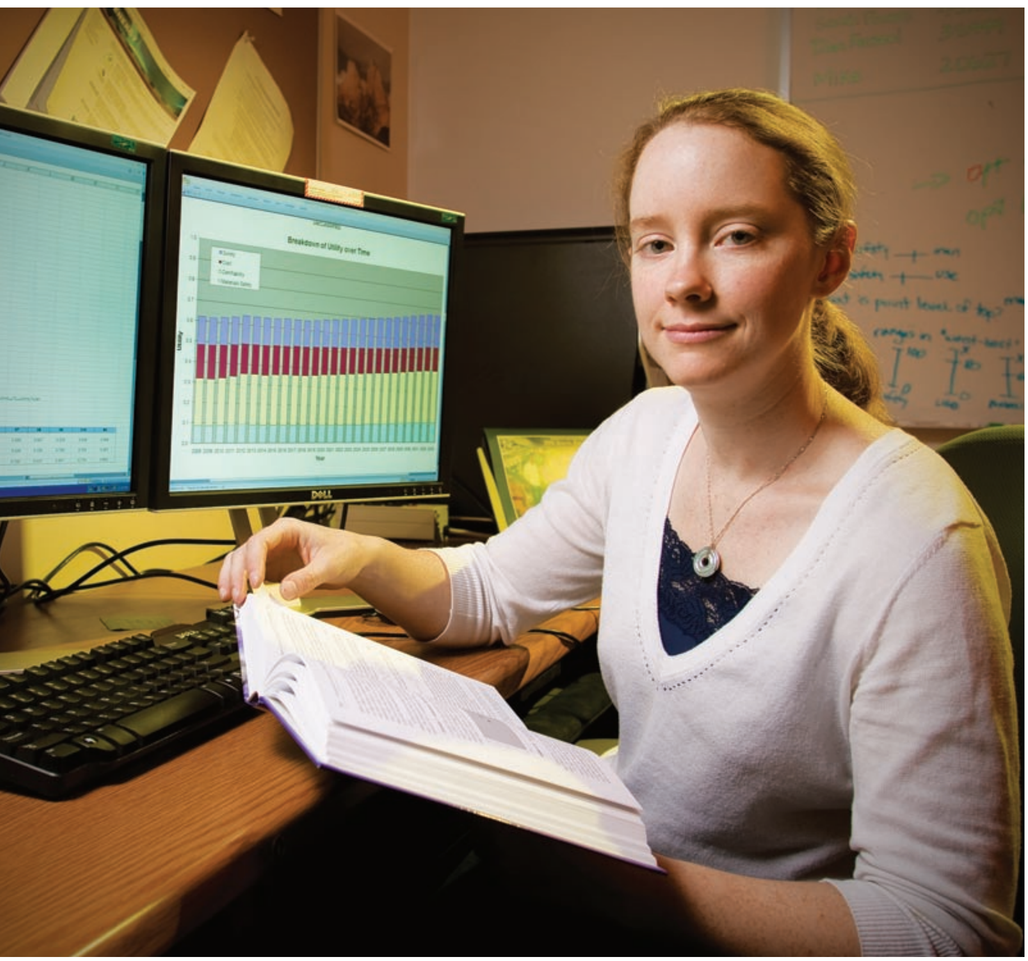


Susan Zimmerman loads a sample wheel into the ion source of an accelerator mass spectrometer.

or other macrofossils; combusts it into carbon dioxide gas; and then catalyzes the gas into graphite powder. The powder is pounded into aluminum sample targets, which are arranged with standard targets and blanks in a sample wheel and loaded into the spectrometer. A wheel with up to 50 unknown samples takes 8 to 12 hours to analyze, and the Laboratory's Natural Carbon Group, which includes Zimmerman, runs 2 to 3 wheels a week. With the high-precision accelerator mass spectrometer, Zimmerman can determine a sample's radiocarbon age to within 20 years.

Once the radiocarbon dates are calibrated to calendar years, Zimmerman and her colleagues establish a chronology for the paleoclimate records from the original core or outcrop. This record is then compared to other sources of ancient climate information, such as tree rings, to develop a regional picture. Combining well-dated paleoclimate records from statewide sites, Zimmerman will create time-slice maps of wet and dry patterns in California in 100-year intervals. In the last phase of her project, she will analyze spectra of the paleoclimate records to look for influences from mechanisms such as the El Niño climate pattern and the Pacific Decadal Oscillation, the long-term surface fluctuation of the Pacific Ocean.

"The Laboratory offers me the opportunity to work with many people in my field," says Zimmerman. This relationship with colleagues benefits everyone involved. Not only does Zimmerman get to do field work in new places and handle a variety of samples, but she also provides researchers statewide with data that might otherwise not be available to them. In addition, the data collected in her project will help strengthen the Laboratory's climate model predictions. With improved models, decision makers can better prepare for what research indicates will be a drier California in the next several decades.



Carol Meyers provides mathematical modeling expertise to several Laboratory programs.

Determining Cause and Effect

Although a native of the San Francisco Bay Area, Carol Meyers never thought her studies in operations research would lead to a career at a nuclear weapons laboratory. Prior to earning a Ph.D. from the Massachusetts Institute of Technology, Meyers spent two summers working with the National Security Agency in Maryland. While there, she began applying her skills to government projects, which led to her joining the Laboratory two-and-a-half years ago. She has since contributed to projects for Weapons and Complex Integration and Global Security and has spent time on LDRD-funded research. "I enjoy being involved in multiple areas of the Laboratory," says Meyers. "I have a lot of flexibility to work on different projects and that has been fun for me."

Working with Livermore scientists Cliff Shang, John Lathrop, Victor Castillo, and Lee Glascoe, Meyers applies mathematical modeling to help evaluate critical decisions. For example, she recently generated cost–benefit models that compare options associated with the National Nuclear Security Administration's (NNSA's) efforts to transform the nuclear weapons complex. "Such modeling illustrates how different choices can affect the complex as a whole," says Meyers, "and, thus, helps NNSA make decisions regarding the nuclear enterprise."

To develop the models, Meyers and her colleagues consult with relevant decision makers to understand the problem being addressed. In a stockpile cost model, one issue concerned whether to fix, replace, or dismantle different types of warheads before they reach the end of their lifetimes. The team identified the problem's variables and any limitations, such as the costs associated with each action, the yearly overall maintenance for a warhead type, and the maximum allowable cost. "Once we have the variables, we establish an objective, for instance, minimizing overall maintenance," says Meyers. Specialized mathematical computer programs then process the data and provide results.

In another project, called MARS (Modeling the Adversary for Responsive Strategy), Meyers is helping Global Security assess different countermeasures against terrorist activity. The MARS model incorporates intelligence data and output from systems such as the Joint Conflict and Tactical Simulation. (See *S&TR*, April/May 2009, pp. 16–22.) "We try to find out who the bad guys are, determine their motivations, and quantify damages that could result from a possible attack," says Meyers. "We then use these data to gauge the effectiveness of countermeasures." This work is related to Meyers's efforts on an LDRD project to model higher adaptive systems in which adversaries change their behavior in response to detection or prevention activities.

Meyers's enthusiasm for her work is palpable. She finds her projects challenging and welcomes the opportunity to learn more, such as participating in the Weapons Intern Program at nearby Sandia National Laboratories. "People at Livermore and Sandia understand the need to pass important knowledge and skills to the next generation of scientists," says Meyers, who plans to join the Laboratory's scientific staff once she completes her postdoc term.

"I never thought I would be involved in this kind of work," she says. "Coming from a liberal background, my family and friends were shocked that I decided to work for a nuclear weapons laboratory. However, I explain that what I am doing is helping to secure a smaller, safer, and more reliable nuclear weapons complex."

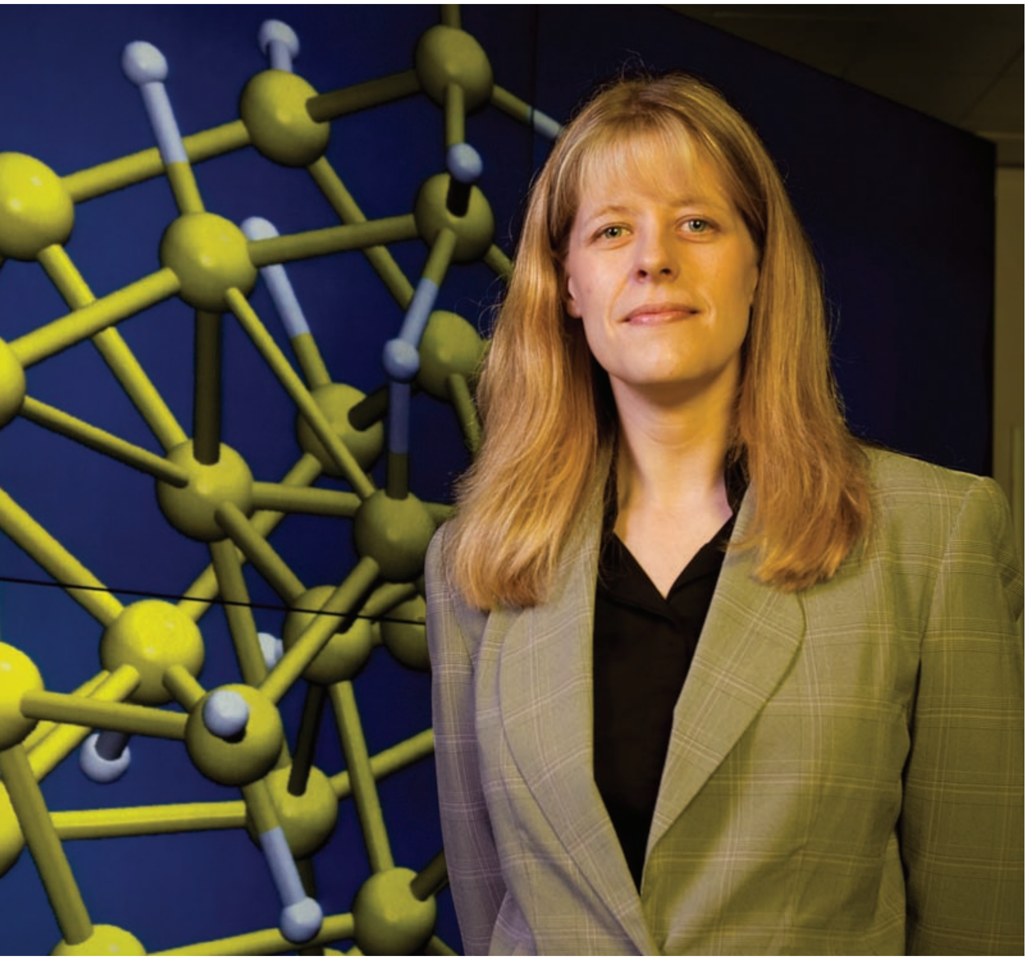
Andrew Cunningham applies three-dimensional modeling to simulate the formation of high-mass stars.

The Life of a Star

Livermore scientists have long been interested in understanding the origins of the universe and celestial bodies such as stars and other solar systems. Andrew Cunningham, who received a Ph.D. in astrophysics from the University of Rochester, is helping researchers improve their understanding of these complex stellar phenomena. Like other postdocs at the Laboratory, Cunningham works on multiple projects. In one project, he uses three-dimensional (3D) models to simulate the formation of stars whose masses are over 20 times greater than that of the Sun.

Star formation begins when a protostellar core draws in gases as it rotates about its axis. Eventually, the dense core collapses into a rapidly rotating accretion disk, similar to the way figure skaters spin faster as they bring their arms closer to their bodies. Gas falls through the disk and feeds the nascent star growing at the disk's center. As a result, gravitational attraction increases, and the star becomes more massive. Throughout this process, radiation emitted from the star's core is pushed outward, opposing the force of gravity and slowing accretion.

Unlike their low-mass counterparts, high-mass stars achieve thermonuclear burn while they are still accreting. Once a star grows to 20 times the mass of the Sun, the outward radiation force becomes strong enough to overcome the inward



Heather Whitley uses the Laboratory's advanced computing resources to study nanomaterials.

gravitational pull. "Researchers expected this process to stop accretion and limit stellar mass to at most 20 times that of the Sun," says Cunningham. "However, stars more than 100 times the Sun's mass have been observed—a phenomenon that is difficult to explain." Simulations by Cunningham, Livermore physicist Richard Klein, and collaborators Christopher McKee from the University of California (UC) at Berkeley and Mark Krumholz from UC Santa Cruz indicate that fluid instabilities in the core free radiation to move outward while still allowing gases to reach the disk.

Previous researchers produced 2D simulations that depicted the rotation of the star and the effects of the accretion disk. "In 2D, we could see how the star collapses and the disk builds and then shields itself from the radiation, creating a gas-scattering phenomenon toward the poles," says Cunningham. The 3D simulations indicate that this gas around the axis inflates radiation-filled bubbles and pushes them out from the core. The bubbles' walls capture the gas and become a mechanism for moving it into the accretion disk.

In 3D, Cunningham and his colleagues can observe gravity, radiation, and fluid dynamics interacting to create these massive stars. In addition, because 3D simulations can depict asymmetric processes, the team can see how fragments of the accretion disk become a binary star within the core and how this second star affects the formation of the high-mass star.

Cunningham runs simulations on the Datastar system at the San Diego Supercomputer Center, using the ORION code. "We start by inputting a slow, rotating dense core of gas into the simulation," he says, "and evolve the system according to a mathematical description of physical processes." ORION applies a technique called adaptive-mesh refinement in which individual grid points, called voxels, are continuously refined as the simulation progresses, which improves grid resolution. "We achieve very high-fidelity results in 3D by concentrating the computational effort where it is most needed," says Cunningham. Focusing the simulation on specific areas of interest reveals gravitational, radiative, and hydrodynamic processes of star formation that would otherwise remain unseen.

For Cunningham, working at Livermore has enabled him to apply his knowledge of computation and astrophysics to a broader spectrum of research. "The Laboratory is conducting ambitious research," he says. "It's a privilege to be part of that work."

A Closer Look at Nanomaterials

Computer simulations also play a significant role in helping researchers understand the functions of materials and living organisms. Since arriving at the Laboratory a year and a half ago, postdoc Heather Whitley has worked with scientists Eric Schwegler and Tadashi Ogitsu using Livermore's advanced computing resources to study the properties of nanomaterials under pressure, the effects of surface structure on the x-ray absorption spectra of a nanomaterial, and materials designed for quantum computers.

Whitley received a Ph.D. in theoretical chemistry from UC Berkeley. Her initial research at the Laboratory focused on simulations of nanometer-size quantum dots—semiconductors with electrons that are spatially confined because of their small size. Her focus is on understanding how the size of a nanoparticle affects its structural phase transitions and optoelectronic properties, and whether those effects can be used in novel applications.

When a material shrinks to nanometer size (10^{-9} meters), its surface has an increased influence on its physical and optical properties as well as its crystalline structure. External conditions, such as applied pressure, further modify this structure. In a nanometer-size material, these changes can affect how the material functions in a particular application. Using quantum mechanical simulations, Whitley examined the size dependence of pressure-induced structural phase transitions in silicon quantum dots.

"Understanding fundamental properties at a microscopic level is key to developing new technologies based on semiconductor nanomaterials," says Whitley. In addition, she is collaborating with David Prendergast and other researchers from Lawrence Berkeley National Laboratory to calculate the x-ray absorption spectra of cadmium–selenium nanomaterials. Both of these studies will help scientists better understand the surface structure of nanomaterials on a microscopic level.

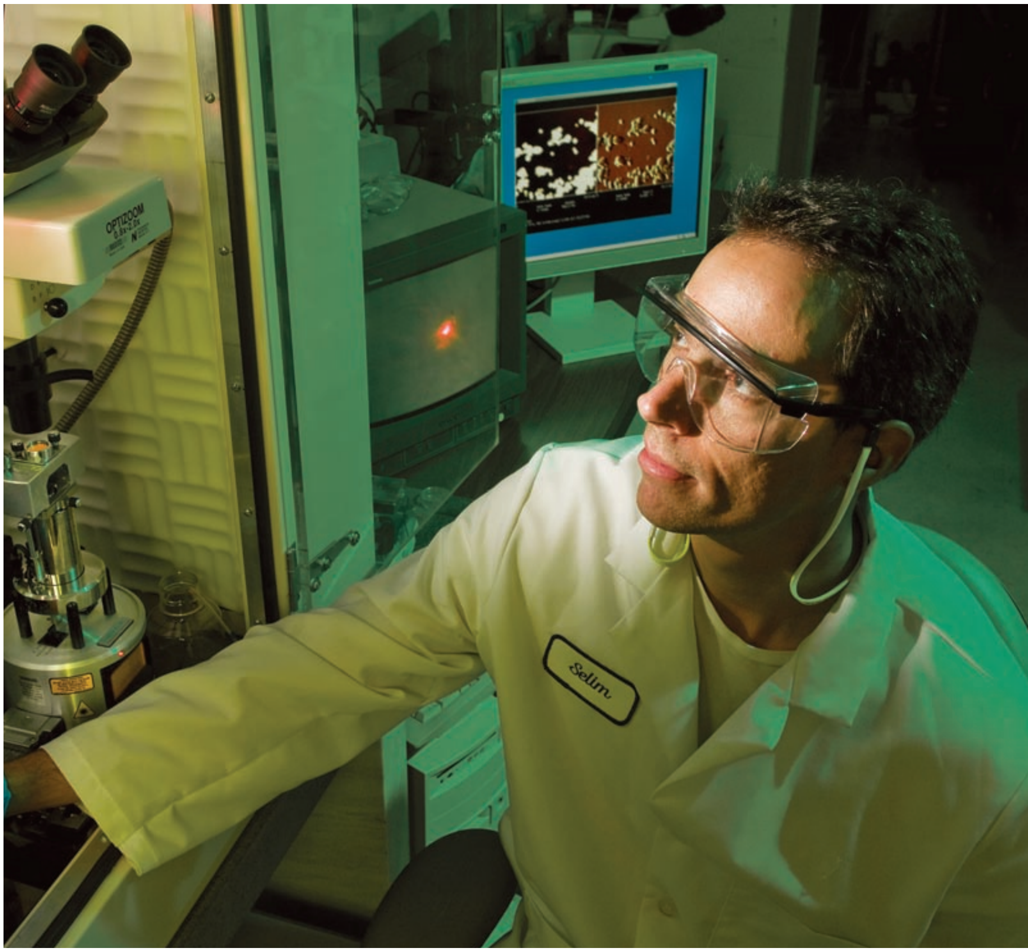
Whitley is also working with the Berkeley Quantum Information and Computation Center at UC Berkeley on a detailed computational analysis of materials for quantum computing. "A major barrier to developing quantum computers is decoherence, a process by which information encoded in a quantum state is lost because of interactions between the quantum system and its surroundings," says Whitley.

In an earlier project, the Berkeley group, which is led by professor K. Birgitta Whaley, used both the electron and nuclear spin states of a single phosphorus-31 donor atom in silicon to study an implementation of quantum computing. The group's findings suggest that the donor electron spin state, which has a fast response to an external field, could be used to perform fast quantum operations. Information encoded in the electron spin state could be transferred to the nuclear spin state, which has a longer lifetime, to enable efficient readout of quantum information. Collaborators at Lawrence Berkeley are also investigating the proposed design to determine which materials are suitable for building a quantum computer.

Working with professionals in her field has opened Whitley's eyes to its many possibilities. "I've seen what science is like outside academia," she says. "Plus, I've had an opportunity to use some of the most advanced computational equipment in existence. I don't think I could have ended up in a better place."

Understanding Crystal Growth

After receiving a Ph.D. in chemical engineering from Virginia Polytechnic Institute and State University (Virginia Tech), Selim Elhadj has spent the last three years at Livermore contributing to such diverse programs as NIF and biosciences. "I was brought to the Laboratory because of my knowledge of crystal growth processes, which are essential for understanding the structural dynamics of nonlinear optical materials and, surprisingly, biological membranes," says Elhadj. Using atomic force microscopy (AFM), he helped develop a method for mitigating damage on laser optics and characterized the dynamics of surface processes in spores and



Selim Elhadj's expertise in crystal growth processes supports a diverse range of Laboratory programs.

bacterial membranes exposed to different environmental perturbations.

In AFM, a nanometer-size pointed tip is moved across a substrate in a raster pattern. The amount of force on the tip changes as it passes over variations, such as scratches or elevated areas on the substrate's surface, which then deflect the tip. AFM records the deflections and reconstructs a complete topography of the surface.

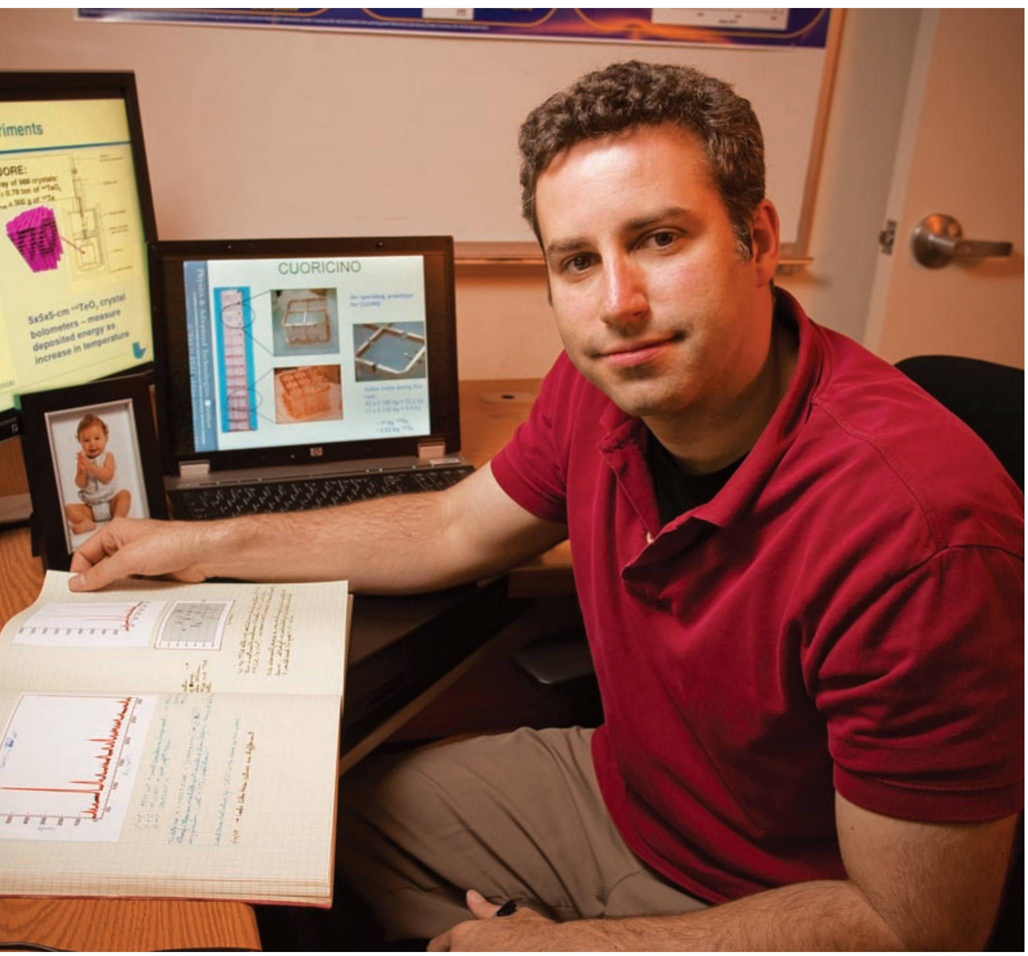
When a substrate is exposed to a solvent-containing atmosphere, a nanometer-thin layer of solvent and a meniscus form where the tip contacts the substrate surface. Elhadj and his colleagues discovered that this approach provides a mechanism by which ions within the material can be transported and redistributed to dissolve mounds and fill in grooves on a material's surface.

In an LDRD-funded study, Elhadj, Vaughn Draggoo, Alex Chernov, and Jim De Yoreo placed a laser-damaged potassium–dihydrogen–phosphate (KDP) crystal substrate into a tightly controlled atmosphere. As the meniscus passed over imperfections in the crystal, KDP molecules were dissolved from convex features and precipitated in concave ones. This redistribution of material was thermodynamically driven and well predicted by a form of the Gibbs–Thomson law, which relates surface curvature to vapor pressure and chemical potential. Says Elhadj, "The mitigation method relies on the shape-dependent solubility of the features, the contrast in their local solubility, and the molecular fluxes within the solvent layer."

Elhadj has also worked with Ibo Matthews and Steven Yang to research methods that will mitigate defects in silica optics by using lasers to melt and vaporize silica. "We used thermographic techniques to measure the temperature of the laser-exposed surfaces," he says. "We then included these measurements in models to predict how the optical materials change and to build diagnostic tools for process control. Measuring the temperature is essential because it represents the driving force of the observed changes relevant to laser-based mitigation."

In a project funded by the Department of Energy and other government agencies, Elhadj and Alex Malkin used AFM to characterize bacterial spores and study structural dynamics of cell surfaces at subnanometer resolution. "Bacteria derive many of their characteristics from their environment," says Elhadj. "We can measure their structures to deduce formulation signatures, for example, to determine if bacteria grew in their natural environment or were manufactured."

AFM is an excellent tool for studying extremely small organisms because spore formulation can be observed in vivo using high-resolution images. "AFM is the only technique that can provide structural information at the scales we are interested in and within relevant environments," says Elhadj. As a result of his efforts, Elhadj has helped expand AFM as a tool for mission-related applications. In doing so, he has deepened the Laboratory's understanding of complex biological crystal growth processes.



Lawrence Fellow Nicholas Scielzo is working on an international project to detect a rare decay process.

A Detector for a Rare Phenomenon

A small subset of postdocs comes to Livermore as part of the Lawrence Fellowship Program. (See *S&TR*, November 2002, pp. 12–18.) These individuals have the freedom to choose the projects they work on during their three-year term. One such postdoc is Nicholas Scielzo, who received a Ph.D. in physics from UC Berkeley. At the Laboratory, he splits his time between three nuclear physics projects, one of which involves detecting an extremely rare radioactive process known as neutrinoless double-beta decay.

In standard double-beta decay, two neutrons in a nucleus are converted to two protons, emitting two beta particles and two neutrinos that share the energy generated from the decay. In neutrinoless decay, the neutrinos annihilate each other instead of being emitted, and the full energy—a little over 2 megaelectronvolts—is carried away by the beta particles. "However," says Scielzo, "this decay can only occur if a neutrino and its antimatter, the antineutrino, are the same particle." In a project funded by the Department of Energy's Office of Science and LDRD, Scielzo is working with U.S. and Italian collaborators to build an extremely sensitive detector to identify this rare decay mode.

CUORE, the Cryogenic Underground Observatory for Rare Events, will be a 1-ton detector located within Italy's Gran Sasso mountain group. The detector will contain an array of nearly 1,000 tellurium dioxide crystals, each a 5-centimeter cube. Tellurium-130 is one of the few isotopes that emit two neutrinos through double-beta decay and thus could theoretically undergo the neutrinoless decay process. The crystals will be cooled to 0.01 kelvins above absolute zero using dilution refrigeration. "At this temperature, each crystal's heat capacity is small enough that the energy from a single radioactive decay within the crystal will be detected," says Scielzo. Sensitive thermometers outside the crystals will indicate a change in temperature, which the team will then use to calculate the decay energy.

As part of his research, Scielzo tests the raw materials used to make the crystals and the shielding for the detector. He also works with vendors to ensure that crystals meet the team's strict specifications. "We look for the most radio-pure materials, those with little to no radioactive background," says Scielzo.

Excess radioactive decay would overshadow the unusual signal they are trying to detect. The detector is surrounded by 1,400 meters of rock overburden to protect it from cosmic muons. Radio-pure shielding must be added to eliminate background radiation from the surrounding environment. Scielzo also applies his knowledge of particle physics to help CUORE researchers interpret the data from the device and develop new detection methods. "Currently, I am researching tellurium-120, which could also undergo the decay," says Scielzo.

CUORE must run for up to five years to collect enough data for accurate analysis. However, researchers on the project know that what they may find is well worth the wait. "The neutrinoless double-beta decay experiments at CUORE have the potential to reveal interesting properties of neutrinos that no other experiments have been able to show," says Scielzo. In addition to proving that the neutrino and its antimatter are the same particle, these experiments could help identify the neutrino mass hierarchy and scale and provide details to explain why matter dominates over antimatter in the universe. "The experiments won't tell us everything we want to know about the formation of our universe," says Scielzo, "but they could provide one component of the larger explanation."

A Mutually Beneficial Relationship

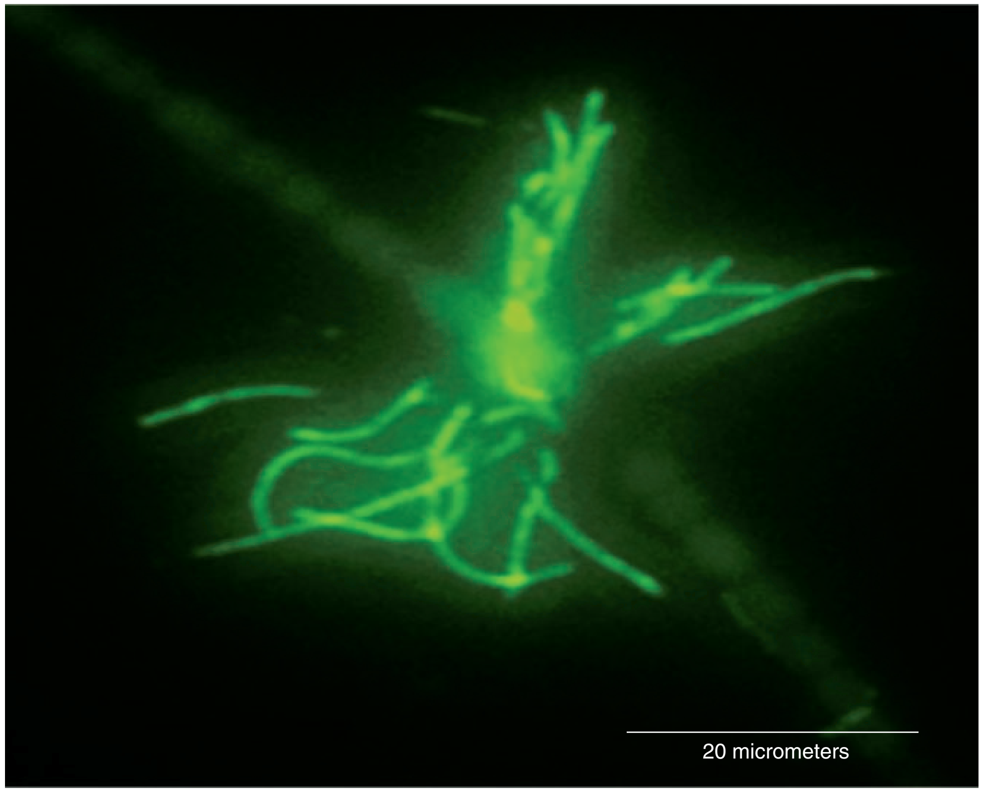
For decades, postdocs have lent their energy and talents to the Laboratory's scientific endeavors, and this tradition will continue into the foreseeable future. Through the Postdoc Program, researchers can apply their skills and expand their knowledge, and the Laboratory maintains a valuable mechanism for recruiting talented scientists and engineers. "The high-quality work of our postdocs enhances the great science performed at the Laboratory," says Kulp. "We are always mindful of how lucky we are to have them working here." They truly are exceptional people producing great science.

—*Caryn Meissner*

Key Words: accelerator mass spectrometer, atomic force microscopy (AFM), climate change, Cryogenic Underground Observatory for Rare Events (CUORE), high-mass star, Institutional Postdoc Program Board, mathematical modeling, nanoparticle, National Ignition Facility (NIF), neutrinoless double-beta decay, particle physics, quantum computing, stockpile stewardship.

For further information contact Kris Kulp (925) 422-6351 (kulp2@llnl.gov).

Revealing the Identities and Functions of Microbes



A new imaging technique combines fluorescent in situ hybridization (FISH) analysis, such as the image shown here, with nanometer-scale secondary-ion mass spectrometry, allowing researchers to decipher the interrelationships of different species. The two species in this FISH image are filamentous *Anabaena* cyanobacteria (barely visible) and *Rhizobium* bacteria (darker green).

SINCE they emerged more than 3 billion years ago, microbes—unicellular organisms such as bacteria—have populated Earth in abundance, conquering every nook and cranny of its surface and subsurface and the tissues of more complex life forms. Their ability to absorb a wide range of substances, most unrecognizable as food to humans, for basic metabolism has led the Department of Energy (DOE) to investigate using microbes to develop biofuels, clean up toxics, and sequester carbon. Researchers also want to study the interactions between disease-causing microbes and native microbe populations in humans, such as the processes that lead to tooth decay.

However, to exploit microbial traits, scientists must better understand their growth and metabolism. "We want to determine how microbes react under different environmental conditions and how they could be engineered to perform useful functions," says environmental microbiologist Jennifer Pett-Ridge in Livermore's Physical and Life Sciences Directorate. With funding from Livermore's Laboratory Directed Research and Development Program and DOE's Office of Science, Pett-Ridge and her colleagues Peter Weber, Xavier Mayali, and Steve Singer have worked with their collaborators at Stanford University to develop an imaging technique that identifies the microbes responsible for specific metabolic processes.

The team's imaging technique, called elemental fluorescent in situ hybridization (El-FISH), combines stable isotope probing with nanometer-scale secondary-ion mass spectrometry (NanoSIMS). NanoSIMS can image trace components with a spatial resolution of 50 nanometers. Laboratory researchers use it for studies ranging from nuclear forensics to cosmochemistry. El-FISH provides even more information, showing which microbes use chemicals labeled with isotopes. The new technique thus allows researchers to study microbes in diverse environments, revealing the often-complex interrelationships of different species comprising microbial communities.

Creating Chemical Images

NanoSIMS instruments scan the surface of a sample with a stream of energetic ions. These ions generate secondary ions, which are extracted by an electric field, sorted by mass, and detected. Only 18 NanoSIMS instruments exist in the world. Livermore's machine is one of three in the nation used for biological imaging.

"A NanoSIMS instrument is similar to a light microscope," says Pett-Ridge, "but it is tuned to specific ions to re-create a chemical image instead of a light image." In this way, the technique reveals which cells—and exactly where in those cells—stable isotopes are incorporated.

Stable isotopes are forms of an element containing one or two extra neutrons. They are not radioactive, and cells assimilate them in exactly the same way as their more common forms. Stable isotopes that are rare in nature serve as elemental tags.

For example, the carbon-12 and nitrogen-14 in a compound can be replaced with carbon-13 and nitrogen-15, respectively, and the new mixture added to microbial systems ranging from a single species to hundreds of species. A NanoSIMS instrument tuned to these rare isotopes can locate the microbes that use the labeled compound.

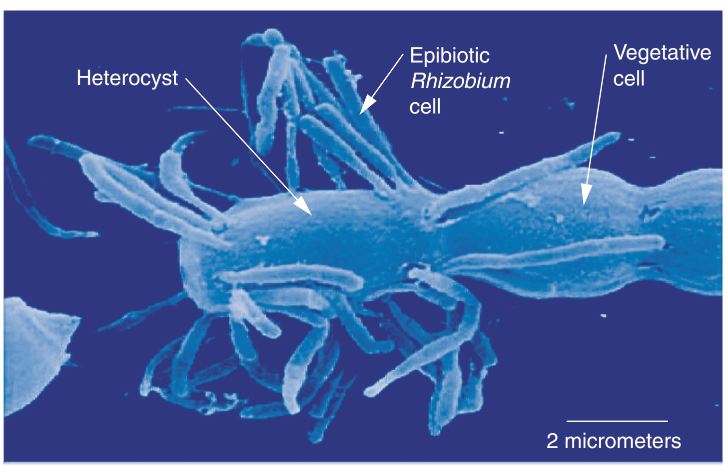
El-FISH combines NanoSIMS imaging with a variant of fluorescent in situ hybridization (FISH), a technique developed in the 1980s by Livermore bioscientists. FISH analyses involve attaching fluorescent dyes to short pieces of DNA, called probes, which bind to complementary sequences of chromosomes in a targeted species. The technique can reveal the identities and locations of different microbes existing in complex communities.

The twist of El-FISH is that an elemental tag, such as fluorine, attached to the probe is imaged in NanoSIMS along with the stable isotopes. The cellular abundance of fluorine or bromine measured following the El-FISH procedure typically exceeds natural background concentrations by up to 180-fold in the targeted species and is easily picked up in NanoSIMS images tuned to fluorine or bromine. "With our technique, we can look at several elements or isotopes at the same time by selectively tuning the NanoSIMS instrument," says Pett-Ridge. "First, the carbon-13 and nitrogen-15 signals give us information about how stable isotopes are metabolized. The fluorine or bromine signal then identifies the organism performing the metabolism."

One of the first imaging applications will be to characterize the roles of microbes living in hypersaline microbial biofilms or mats. These highly diverse, layered microbial communities develop on the surface of sediments in marine estuaries and salt ponds and can generate hydrogen gas. In a DOE-funded collaboration with researchers at the National Aeronautics and Space Administration's Ames Research Center and Stanford University, Pett-Ridge and her colleagues add compounds containing carbon-13 to microbial mat communities. They then follow how the bacteria take up and break down these compounds to learn about the critical links between carbon and nitrogen nutrients and the generation of hydrogen gas.

With other DOE funding, the team is partnering with Lawrence Berkeley National Laboratory and Louisiana State University to characterize the complex microbial community dwelling in the hindgut of wood-eating beetles. Like termites, these beetles have developed a symbiotic relationship with a community of gut microbes whose combined enzymes digest the complex polysaccharides and lignins of plant cell walls and produce acetate, methane, and hydrogen gas. Understanding how these microbial populations interact to break down cellulosic materials could aid large-scale industrial projects planned to convert biomass such as wood chips into hydrogen and methane biofuels.

Another promising effort is attempting to understand the metabolism of different bacteria responsible for chronic periodontitis, the leading cause of tooth decay and loss in humans. Periodontitis is linked to several bacterial species, including one called human TM7. Defining the role of TM7 during disease progression requires characterizing its ecologic niches in the mouth and revealing its metabolic functions, a task well suited to El-FISH. The dental disease research is being conducted in conjunction with researchers at Stanford University and the Veterans Affairs Palo Alto Health Care System.

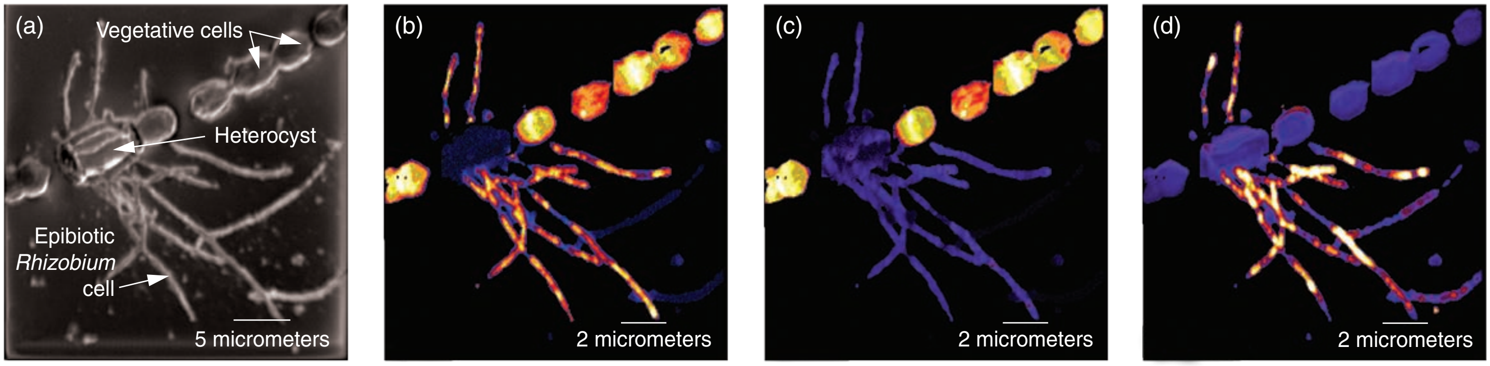


In this micrograph, *Rhizobium* cells appear as rods radiating from the junction between *Anabaena*'s heterocysts, which convert atmospheric nitrogen to ammonium, and vegetative cells, which conduct photosynthesis. (Courtesy of Bradley S. Stevenson and John B. Waterbury, from "Isolation and Identification of an Epibiotic Bacterium Associated with Heterocystous *Anabaena* Cells," *Biological Bulletin*, 2006, pp. 73–77.)

Studying a Microbial Community

In a proof-of-concept demonstration of the El-FISH technique, the research team studied a two-species community, or coculture, of filamentous *Anabaena* cyanobacteria (blue-green algae) and epibiotic (living on the surface of another species) bacteria from the family *Rhizobium*. Although many cyanobacteria species are free-living, some are closely associated with other organisms, including plants, algae, fungi, and other bacteria. Understanding these associations provides important insights into the ways microbes metabolize and share nutrients.

Filaments of *Anabaena* cyanobacteria consist of two kinds of cells: Vegetative cells conduct photosynthesis, converting atmospheric carbon dioxide to oxygen. Heterocysts fix atmospheric nitrogen, converting nitrogen gas to ammonium. A typical cyanobacteria filament has 15 to 20 vegetative cells between each heterocyst. Scientists have detected neither photosynthesis nor nitrogen fixation in *Rhizobium* cells when grown on their own. However, electron microscope images indicate that when these cells are grown with *Anabaena, Rhizobium* rods radiate from the junction between *Anabaena's* vegetative and heterocyst cells. (See the figure at left.)



Elemental fluorescent in situ hybridization (El-FISH) was used to examine (a) a chain of eight *Anabaena* cyanobacterial cells with elongated *Rhizobium* bacterial cells attached. (b) Fluorine identifies the organisms. Isotope images show the relative uptake of (c) newly fixed carbon (carbon converted from carbon dioxide to organic materials) and (d) newly fixed nitrogen (converted from its atmospheric gas to nitrogen compounds). Isotope enrichment ranges from yellow (maximum) to orange, red, purple, and blue.

To better examine this two-species system, the team imaged the assimilation and flow of nutrients, in particular, the exchange of carbon and nitrogen molecules, between the two bacteria. A succession of NanoSIMS images (shown above) reveals that carbon-13 is incorporated into cells through photosynthesis and nitrogen-15 through nitrogen fixation. The team found that heterocysts export fixed nitrogen to vegetative cells, but only vegetative cells incorporate fixed carbon (from carbon dioxide) into carbon compounds. In addition, the team's results suggest that *Anabaena* cells transfer significant quantities of both carbon and nitrogen compounds to *Rhizobium* cells. Most of this nutrient exchange appears to occur at the junction between heterocysts and vegetative cells, the place where *Rhizobium* cells attach.

Tracking Isotopes within Cells

The researchers also studied the accumulation and distribution of isotopes when either nitrogen fixation or photosynthesis was inhibited with materials that inactivate essential cell enzymes. These experiments strengthened their conclusion that *Rhizobium* cells cannot perform nitrogen fixation or photosynthesis. Therefore, the stable isotopic labels (carbon-13 and nitrogen-15) found in *Rhizobium* must be derived from the host.

According to Pett-Ridge, this high degree of attachment specificity at the heterocyst–vegetative cell junction indicates *Rhizobium* cells possess sensors that can discriminate between cell types. It remains unclear if *Rhizobium* has deleterious effects on the host (parasitism) or provides benefits (symbiosis).

El-FISH is attracting interest from biological researchers worldwide. Over the next few years, scientists may use the technique to engineer bacteria for producing biofuels or to study microbial communities and host–pathogen interactions in nature and the human body. The methodology could also advance understanding of how microbes break down and sequester carbon dioxide in the soil, immobilize toxic metals, and biodegrade hazardous organic pollutants. Clearly, organisms that have evolved over 3 billion years may have some secrets to help the most recent arrival on Earth—humankind.

—*Arnie Heller*

Key Words: biofuels, elemental fluorescent in situ hybridization (El-FISH), microbe, nanometer-scale secondary-ion mass spectrometry (NanoSIMS), stable isotope.

For further information contact Jennifer Pett-Ridge (925) 424-2882 (pettridge2@llnl.gov).

A Laser Look inside Planets

TRADITIONAL lasers, gas guns, and other dynamic high-pressure testing methods launch an instantaneous shock into a target, resulting in rapid heating, which at high pressures causes the material to melt. A new technique called laser-driven ramp compression zaps the material with a carefully tailored laser shot. Laser-driven ramping can achieve high states of compression while simultaneously keeping the target material relatively cool so scientists can examine the material under high pressures. The "loading" time of laser ramp compression is just a few nanoseconds, or 10 times faster than that of the fastest alternative.

Under extremely high pressures, the target material may remain in its initial phase, or it may change from a solid to a liquid or from one solid phase to another. To date, laser-ramp-compression experiments have achieved pressures up to 1,400 gigapascals (GPa), or 1.4×10^{12} pascals. For reference, ambient air pressure is 100,000 pascals, and the pressure at the center of Earth is about 350 GPa.

Shock experimental methods reveal a snapshot of part of a phase transition. Ramp compression offers the first continuous view of the phase transition and thus will help scientists better understand the physics of solids at extreme conditions. "We now can see how quickly the transition mechanisms happen," says physicist Ray Smith, who leads the ramp-compression research team in Livermore's Physical and Life Sciences Directorate.

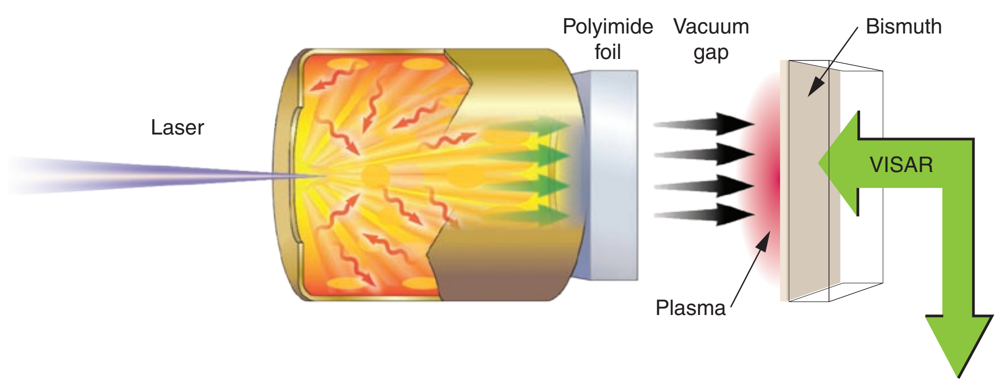
Because of these unique attributes, ramp compression is the only tool that will allow scientists to examine the interior structure of exoplanets—planets in other solar systems—that are similar to but larger than Earth. More than 250 exoplanets have been discovered since 1995, but most are huge gas giants similar to Jupiter and Saturn. In the last few years, detection and survey methods have improved such that smaller exoplanets and ones closer to their parent star can be found. While our solar system contains only small rocky planets and gas giants, recent discoveries indicate that other solar systems contain a new family of terrestrial planets more massive than Earth but smaller than the gas giants.

These so-called super-Earth planets range from 1 to 10 times the mass of Earth, with pressures at their core from 3,000 to 5,000 GPa. Although ramp-compression experiments have yet to achieve the high pressures at a planet's core, they can re-create the phase transitions occurring well beneath an exoplanet's surface. Scientists can thus use this laser method to test various planetary hypotheses, such as whether Uranus has a solid diamond core.

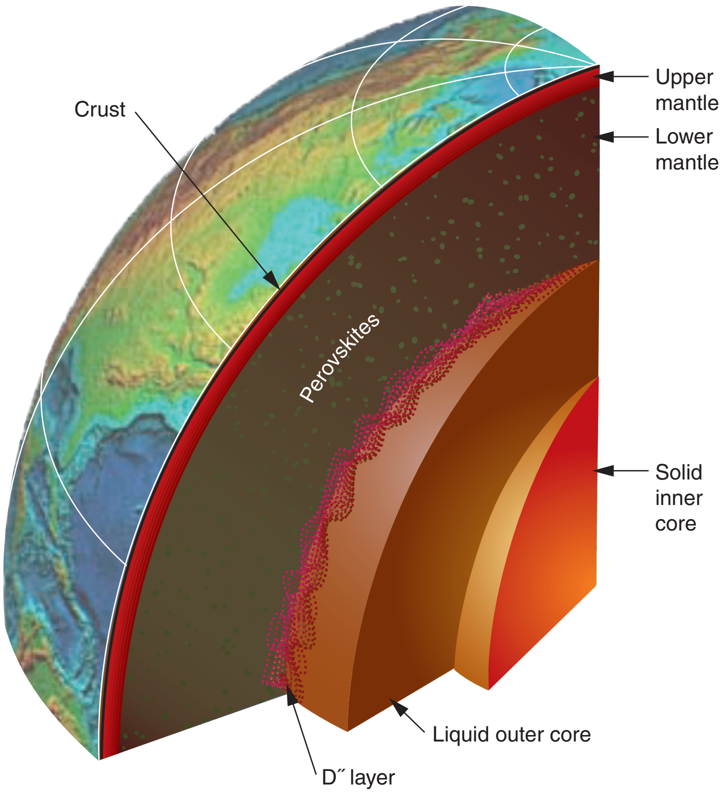
Ramping Up the Method

In 2005, Livermore physicist Marina Bastea performed the first experiments to ramp-compress bismuth. Those experiments were conducted on the Z machine, the x-ray source at Sandia National Laboratories in New Mexico, and the compression rates were about 10 times slower than the rate obtained in subsequent experiments with Livermore's Janus laser.

Since then, Smith's team has developed the techniques and diagnostic tools essential for routine high-pressure ramp-compression experiments. In 2007, the team used one beam of the Janus laser to generate a 150- to 200-joule pulse that strikes a polyimide foil and rarefies it. The polyimide crosses the vacuum gap and hits the bismuth sample, launching a ramp-compression



In ramp-compression experiments on Livermore's Janus laser, the laser beam directs a pulse toward a polyimide foil. The polyimide crosses the vacuum gap and hits the bismuth sample, launching a ramp-compression wave with peak pressure between 8 and 11 gigapascals. A diagnostic called VISAR (Velocity Interferometer System for Any Reflector) records the time history of the compression wave.



Using seismic-wave data recorded during earthquakes and other geologic disturbances, scientists have determined the makeup of Earth's interior. Ramp-compression experiments will offer yet more clues about deep-Earth conditions.

wave with peak pressure between 8 and 11 GPa. (See the figure on p. 22.) A diagnostic tool called VISAR (Velocity Interferometer System for Any Reflector) records the time history of the compression wave.

Bismuth samples are preheated to a range of temperatures, which enables access to different regions of the pressure–temperature continuum and provides insights into the phase-transformation mechanisms. "The pressure at which the phase transition occurs shows a deviation from the crystal's equilibrium value," says Smith. "For the first time, we can see the very brief timescale during which the crystal transforms to a new structural phase."

Subsequent experiments led by Livermore physicist Dave Bradley compressed diamond, a solid phase of carbon, using the higher energy OMEGA laser at the University of Rochester's Laboratory for Laser Energetics. These experiments yielded the highest ramp-compression pressures ever reported, 1,400 GPa, as well as the highest-pressure solid equation-of-state data. Data for pressure versus density indicate that the diamond phase is stable with significant material strength up to at least 800 GPa.

Data Still to Come

The research team has received funding from Livermore's Laboratory Directed Research and Development Program and is now working on a collaborative project to perform more ramp-compression experiments at OMEGA. In addition to Smith and Bastea, this effort includes Laboratory researchers Jon Eggert, Pete Celliers, David Braun, and Ryan Rygg as well as scientists from Washington State University, Princeton University, Carnegie Institution for Science, University of Rochester, and University of California at Berkeley. These new measurements will more carefully define the phase boundaries, kinetics, and thermodynamic properties under deep-Earth conditions, which will help scientists better understand the structure and composition of planetary interiors.

The first shots will compress iron up to about 500 GPa. The team will also examine silica, which serves as an archetype for the dense, highly coordinated silicates that make up planetary interiors. Enstatite, another common mineral in Earth's mantle, transforms to perovskite, the most abundant phase in Earth's vast lower mantle. A series of OMEGA experiments will probe the expected enstatite–perovskite phase change, the perovskite–postperovskite phase change, and any as-yet-unknown phase changes above 200 GPa. The primary diagnostic tools, VISAR and x-ray diffraction, will provide information on the crystal structure of the new phases.

In September, some of the same partners will collaborate on the first ramp-compression experiments at the National Ignition Facility (NIF), the world's most energetic laser system. The first material to be subjected to NIF's high-power beams will be tantalum, which will be compressed to 500 GPa to examine its equation of state. Iron, other heavy metals, and diamond will also be on the receiving end of 96 NIF beams. Says Gilbert (Rip) Collins, a coleader for the NIF experiments, "NIF will enable us to examine the evolution, structure, and internal chemistry of solar and extrasolar planets."

—Katie Walter

Key Words: equation of state, exoplanet, laser-driven ramp compression, OMEGA laser, National Ignition Facility (NIF), phase transformation, super-Earth planet.

For further information contact Ray Smith (925) 423-5895 (smith248@llnl.gov).

In this section, we list recent patents issued to and awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory.

Patents

Oscillation Damping Means for Magnetically Levitated Systems

Richard F. Post
U.S. Patent 7,478,598 B2
January 20, 2009
This method dampens rolling, pitching, or yawing motions and longitudinal oscillations superposed on the normal forward or backward velocity of a moving levitated system.

Electromagnetic Variable Degrees of Freedom Actuator Systems and Methods

Richard C. Montesanti, David L. Trumper, James L. Kirtley, Jr.
U.S. Patent 7,492,117 B2
February 17, 2009
This variable reluctance actuator system simultaneously rotates and translates a moving element by applying a normal-direction magnetic flux on the element. In one arrangement, a swing arm carries a cutting tool at a set radius from the axis of rotation, producing a rotary fast tool servo. The tool motion is parallel to the surface of a workpiece at the point of contact between the cutting tool and the workpiece. An actuator rotates the swing arm such that the cutting tool moves toward and away from the mounted rotating workpiece in a controlled manner, thus machining the workpiece. Position sensors send rotation and displacement information about the swing arm to a control system. The control system coordinates the motion of the fast tool servo with that of a spindle, rotating table, cross-feed slide, and in-feed slide of a precision lathe.

Nucleotide Sequences Specific to *Yersinia pestis* and Methods for the Detection of *Yersinia pestis*

Paula M. McCready, Lyndsay Radnedge, Gary L. Andersen, Linda L. Ott, Thomas R. Slezak, Thomas A. Kuczmarski, Vladinir L. Motin
U.S. Patent 7,494,772 B2
February 24, 2009
Nucleotide sequences specific to *Yersinia pestis* serve as markers or signatures for identifying this bacterium. Forward and reverse primers and hybridization probes derived from the sequences are also used to detect the presence of the bacterium.

Nucleotide Sequences Specific to *Brucella* and Methods for the Detection of *Brucella*

Paula M. McCready, Lyndsay Radnedge, Gary L. Andersen, Linda L. Ott, Thomas R. Slezak, Thomas A. Kuczmarski
U.S. Patent 7,494,773 B2
February 24, 2009
Nucleotide sequences specific to *Brucella* serve as markers or signatures for identifying this bacterium. Forward and reverse primers and hybridization probes derived from the sequences are also used to detect the presence of the bacterium.

Nucleotide Sequences Specific to *Francisella tularensis* and Methods for the Detection of *Francisella tularensis*

Paula M. McCready, Lyndsay Radnedge, Gary L. Andersen, Linda L. Ott, Thomas R. Slezak, Thomas A. Kuczmarski, Elizabeth A. Vitalis
U.S. Patent 7,494,778 B2
February 24, 2009
Nucleotide sequences specific to *Francisella tularensis* serve as markers or signatures for identifying this bacterium. Forward and reverse primers and hybridization probes derived from the sequences are also used to detect the presence of the bacterium.

Awards

Keith Carlisle in Livermore's Engineering Directorate has been named a **Fellow** of the **Institute of Mechanical Engineers**, a professional engineering organization in the United Kingdom. The British-born mechanical engineer has applied his expertise in precision engineering to many critical projects at the Laboratory, such as new manufacturing capabilities for Weapons and Complex Integration and crystal machining for the National Ignition Facility (NIF). Last year, his design for the next-generation shell machine was selected for use in manufacturing pits at Los Alamos National Laboratory.

The **Alameda County Women's Hall of Fame** named Laboratory physicist **Gina Bonanno** as the **2009 Outstanding Woman of the Year** in the science category. A program leader in the NIF and Photon Science Principal Directorate, Bonanno heads the National Ignition Campaign, which is preparing for the first set of fusion experiments on NIF. The Alameda County Women's Hall of Fame was established in October 1993 to recognize outstanding women in the California county for their achievements and contributions to the county and its citizens.

Ruth Tinnacher, a postdoctoral researcher in Livermore's Physical and Life Sciences Directorate, received the **2008–2009 CH2MHILL/ESE Outstanding Graduate Student Award** from the **Colorado School of Mines** in Golden, Colorado, where she earned her doctorate in December 2008. The award is named for its benefactor, CH2MHILL, a global engineering and construction company that acknowledges outstanding contributions of students in the environmental science and engineering graduate program. In her work at the Laboratory, Tinnacher is studying the parameters that affect the environmental mobility of radioactive contaminants in soils and groundwater systems.

Abstracts

Dissolving Molecules to Improve Their Performance

The molecule 1,3,5-triamino-2,4,6-trinitrobenzene, commonly known as TATB, is a high explosive that is nearly invulnerable to significant energy release from plane crashes, fires, explosions, or small arms fire. Because of its inherent safety, TATB is used in nuclear weapons, conventional munitions, and explosives for mining and oil production activities. TATB has not been produced for more than two decades primarily because of environmental regulations. To meet military requirements, the Department of Defense must purchase it from Department of Energy stockpiles until new manufacturing methods are developed. The scarcity of TATB makes recycling the material from old nuclear warheads an attractive option. Livermore scientists have combined 3-ethyl-1-methylimidazolium acetate and dimethyl sulfoxide to develop a solvent system belonging to a class of compounds called ionic liquids. The new system produces TATB crystals with better crystal quality, size, shape, and purity than previous manufacturing techniques have produced.

Contact: Robert Maxwell (925) 423-4991 (maxwell7@llnl.gov).

Exceptional People Producing Great Science

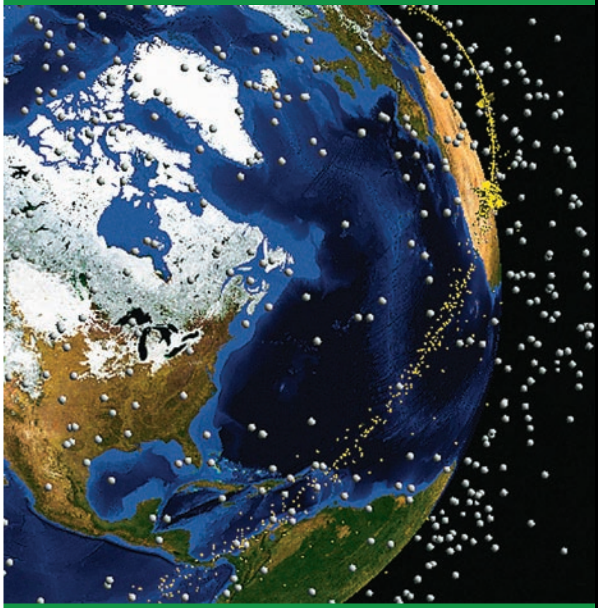
At any given time, Livermore is home to 110 to 150 postdoctoral researchers, or postdocs, who lend their scientific talents to projects in the Laboratory’s four mission-related programs. Postdocs come from all over the country—and in some cases from abroad—within the first five years after receiving a doctoral degree. These exceptional people apply their skills and knowledge in the areas of climate change, stockpile stewardship, astrophysics, nanomaterials, crystal growth, biosciences, and nuclear physics. As part of the Laboratory’s Postdoc Program, they get hands-on experience while working closely with scientific leaders and colleagues in their disciplines. Assignments typically last two to three years. After this initial term, some postdocs remain as Laboratory employees, while others venture out into academia or industry.

Contact: Kris Kulp (925) 422-6351 (kulp2@llnl.gov).

U.S. Government Printing Office: 2009/570-075-71012

Coming Next Issue

Preventing Collisions in Space



The Testbed Environment for Space Situational Awareness is building computational tools to detect and monitor threats to the nation’s space operations.

Also in July/August

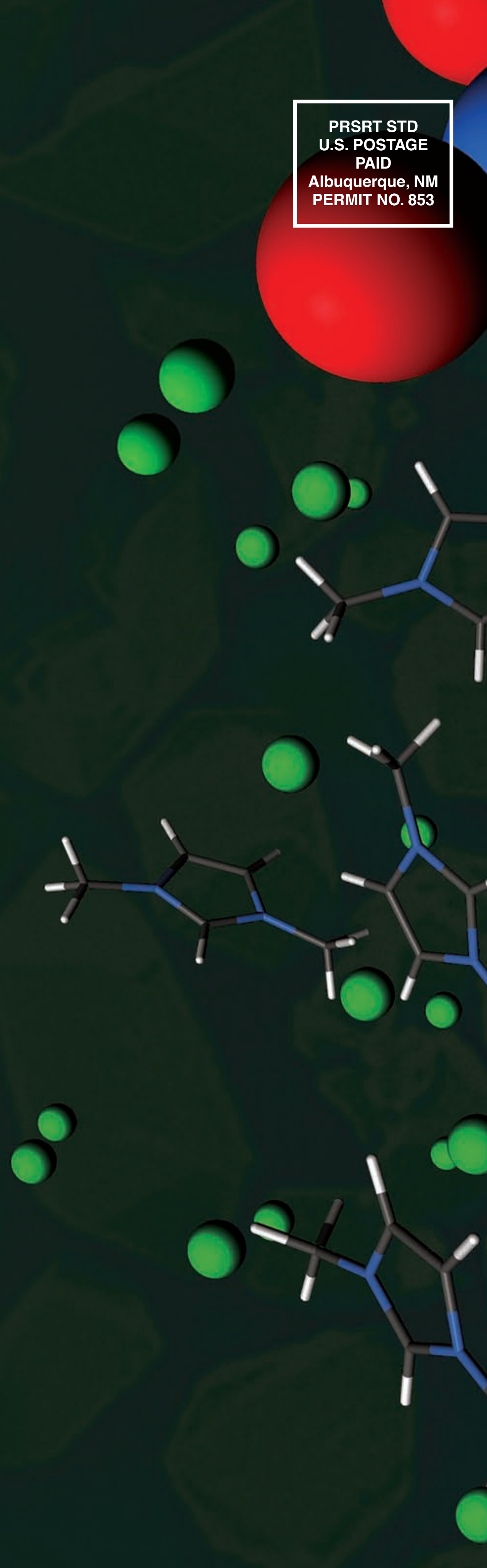
• A new x-ray system images nuclear weapon components in three dimensions, promising unprecedented resolution and clarity.

• Livermore scientists have developed a laser-based method for quickly generating positrons in a laboratory setting.

• Portable medical diagnostic equipment using ultrawideband technology helps first responders evaluate injuries during emergencies.

Science & Technology Review
Lawrence Livermore National Laboratory
P.O. Box 808, L-664
Livermore, California 94551

PRSRT STD
U.S. POSTAGE
PAID
Albuquerque, NM
PERMIT NO. 853



Printed on recycled paper.